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SORPTION PUMPING OF HYDROGEN BY CRYODEPOSITS–SORPTION CAPACITY MEASUREMENT

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ARO, Inc.

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NOTICES

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FOREWORD

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This technical report has been reviewed and approved.

Michael G. Buja 1st Lt, USAF Research Division Directorate of Plans and Technology	Harry L. Maynard Colonel, USAF Director of Plans and Technology

ABSTRACT

The state-of-the-art of cryosorption of hydrogen (H_2) and helium by cold cryodeposited frost is reviewed and summarized in some detail, and the results of additional measurements of the sorption of H_2 by carbon dioxide (CO_2) frosts are reported. It is shown that the sorption capacity of the frost depends upon the conditions at which the frost was formed and upon its temperature history. Frosts formed in a manner to make them porous or disordered are shown to possess greater sorption capacities. It appears that surface diffusion of adsorbed molecules into a disordered frost structure is the basic pumping mechanism. Isotherms for H_2 sorbed by CO_2 frosts formed over a wide range of conditions are presented. Also, the reuse sorption capacity of CO_2 frost is well documented. As a result of the present tests, it is now possible to put the process of frost cryosorption pumping into better perspective and understand the conflicting results of previous experimental investigations.

CONTENTS

TABLE

APPENDIXES

NOMENCLATURE

A	Area
a_o	Lattice constant
C	Capacity, ratio of number of sorbed hydrogen molecules to the number of carbon dioxide molecules deposited in frost
c	Amount of sorbed gas
K	Leak conductance
k	Boltzmann's constant
$\bar{\ell}$	Mean thickness of frost sorbent

M	Molecular weight
m	Mass flow
P	Pressure
P*	Pressure gage output
Q	Amount of gas in torr-liter
$\dot{Q}$	Throughput, torr-liter/sec
S	Pumping speed
T	Temperature
T_s	Supply temperature of helium cryogen
T_r	Return temperature of helium cryogen
t	Time
V	Volume
α	Gage sensitivity factor
ρ	Density

SUBSCRIPTS

a	Gas addition system
add	Added
c	Chamber
deposit	Conditions at time of deposit
f	Frost
f_m	Maximum temperature experienced by frost gas
form	Formation
g	Gas
i	Initial
liq	Liquid
o	Outgassing
s	Sorbent in gas state
sorb	Conditions at time of sorption
sorbate, sorbent	See Appendix II for definitions
v	Vapor
warmed	Intervening condition when frost was warmed

SECTION I
INTRODUCTION

Cryodeposited frosts formed by condensing certain gases (such as carbon dioxide (CO_2), argon (Ar), oxygen (O_2), and nitrogen (N_2)) on surfaces at temperatures between 10 and 20°K have been shown to provide an effective means to pump hydrogen (H_2) (Refs. 1 through 7). Moreover, these frosts will also effectively pump helium (He) if the cryosurface temperature is maintained at 4.2°K and below (Refs. 8, 9, and 10). A summary and assessment of the state-of-the-art of frost cryosorption pumping is given in Section II of this report.

These previous investigations have demonstrated that the pumping speed of frosts for H_2 and He are relatively high; in some cases, as high as 70 percent of the theoretical maximum value. However, there are large differences in the measured values of the sorption capacity, and the maximum amount of gas which may be sorbed is unknown. Consequently, it was apparent that, if improvements could be made in the effectiveness of cryosorption pumps, they would primarily be made in the area of increased sorption capacity. This report describes the results of a number of sorption tests carried out to define factors which influence the sorption capacity of frosts and to determine to what extent the capacity could be increased. Terms used to describe cryosorption phenomena in this report are defined in Appendix II.

SECTION II
A SURVEY OF PREVIOUS FROST CRYOSORPTION STUDIES

As long ago as 1933, Keesom and Schmitt in Holland (Ref. 11) noticed that gaseous helium (GHe) would stick to a glass container cooled to liquid-helium (LHe) temperatures, perhaps because of physical adsorption. In the intervening years, many investigators have reported that the partial pressures of H_2 and He were lower than expected in vacuum chambers containing cryosurfaces cooled to about 20°K.

In 1961 Brackman and Fite (Ref. 12) may have supplied the explanation of these anomalies. While studying the reflection properties of atomic and molecular H_2 from cold surfaces using a molecular beam, they found that cryosurfaces at temperatures below 20°K which were partially covered with water (H_2O) ice were capable of condensing H_2. After a brief study they stated: "...it seems appropriate to suggest that the experimental results indicate either a true adsorption of H_2 to frozen-water surfaces or a trapping of H_2 by simultaneously condensing H_2O vapor or perhaps both."

These investigators presented no data but also reported that H_2O frost at temperatures between 7 and 14°K appeared to pump He, while O_2 was pumped by H_2O frost in the 60 to 90°K temperature range. As a result, they proposed the use of ice pumping as "the world's least expensive method of producing a vacuum." However, Brackman and Fite did not offer any analysis of this pumping phenomenon.

A short time later, Hunt, Taylor, and Omohundro reported the results of a more extensive investigation of this phenomenon (Refs. 1 and 2). These researchers employed a conventional vacuum chamber which contained a small cylindrical cryosurface cooled

with GHe. After the chamber was evacuated to 10^{-7} torr and valved off from its diffusion pump, the cryosurface was cooled to 11°K. A particular gas was then admitted to the chamber forming a thin frost deposit on the 11°K cryosurface. Generally, about 10 to 20 torr-liters of gas were admitted over a 1- to 1.5-hr period, which resulted in an estimated mean cryodeposit thickness of 0.02 to 0.05 μ formed at a very slow rate. However, because of their system geometry, the frost could not have been deposited uniformly over the cryosurface. After the gas addition was completed, H_2 at 300°K was introduced through a palladium (Pd) leak.

These investigators report very high adsorption rates and sticking probabilities of room temperature H_2 on cryodeposit films of Ar, N_2, O_2, H_2O, N_2O (nitric oxide), and CO_2. All of their test results are summarized here in Fig. 1 (Appendix I) which shows the pumping speed of the frost as a function of its capacity[1] to pump H_2. It was observed that the various frosts pumped H_2 at various pumping speeds until they approached saturation; and then the pumping speed diminished very rapidly. They concluded that adsorption was responsible for the pumping action and that pumping ceased once a monolayer of H_2 was formed on the frost. Also, they estimated the adsorption energies were a few hundred cal/mole.

In addition, it was found that the H_2 could be readily desorbed by increasing the frost temperature to 20°K, and, when the frost was cooled again, it would pump almost as well as it did initially. Although this group concluded that adsorption cryopumping, as they called it, of hydrogen was feasible, they apparently did not pursue it further.

The investigation of cryodeposited frost films as sorbents for H_2 apparently lay dormant for the next four or five years. During this time the interest and emphasis shifted to cryosorption in which molecular sieves were used to sorb H_2 (see Refs. 13 through 16, for example). The results of a few studies of H_2 cryotrapping (see Appendix II for definition of terms) also began to appear in the literature (Refs. 17 and 18)[2]. Then, in 1965 the use of H_2O and CO_2 frosts for the cryosorption of H_2 was accidentally rediscovered by Southerlan (Ref. 3) and independently discovered again in 1966 in Russia by Busol and Yuferov (Ref. 4).

Southerlan (Ref. 3) was investigating the cryosorption characteristics of molecular sieves on a large scale in a 7-ft space simulation chamber at the Arnold Engineering Development Center (AEDC). During these tests he intentionally attempted to contaminate a molecular sieve panel at 20°K with H_2O vapor, but found that the H_2O frost had a higher H_2 pumping speed than the sieve material at the same temperature. As a result, he carried out a few additional cryosorption tests with H_2O and CO_2 frosts on a cryopanel at 20.4°K and about 16°K, respectively. It is significant to note that the CO_2 frost deposited at 16°K was warmed to about 28°K and subsequently cooled to 16°K

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[1]The capacity is defined as the number of molecules sorbed divided by the number of molecules predeposited in the frost sorbent.

[2]Some investigators, apparently unaware of Hunt's work, have reported cryotrapping of He and H_2. In retrospect, they may have been witnessing a cryosorption process rather than trapping.

before the sorption test began. Southerlan's data are difficult to compare with those of other investigators because several factors were allowed to vary during the course of a sorption test. However, he concluded that the capacity of CO_2 frost at 16°K to sorb 77°K H_2 was considerably lower than the capacity of 20.4°K H_2O frost to sorb 300°K H_2, which is somewhat surprising, particularly in the light of subsequent tests by Dawbarn (Ref. 5).

Dawbarn continued investigation of cryosorption of H_2 with CO_2 frost at AEDC in a smaller research chamber. His experimental apparatus and procedure were similar to those used by Hunt, et al. (Ref. 2). However, Dawbarn used a GHe-cooled spherical cryosurface situated such that a uniform frost thickness could be obtained, and he deposited frosts of approximate thicknesses of either 0.05 or 1 μ at the same temperature at which the subsequent sorption pumping was carried out. The influence of the temperature of the frost and, to some extent, the temperature of the H_2 were the prime variables studied in this investigation. It was found that the pumping speed (Fig. 2) and capacity of the frost to sorb H_2 significantly increased with decreasing frost temperature; and, at a frost temperature of 25°K, no measurable pumping occurred. The maximum sorption capacities which were achieved during these tests at a chamber pressure of 5×10^{-7} torr are summarized in the following table:

Temperature of CO_2 Cryodeposit, °K	Capacity Number of H_2 molecules Sorbed/ Number of CO_2 molecules in Frost
20	0.005
16	0.020
12	0.125

These studies also indicated in a limited way that the amount of H_2 which could be pumped was proportional to the frost volume, and the pumping mechanism was more complicated than just surface adsorption as suggested by Hunt, et al.

In addition, it was found that N_2 readily contaminated the CO_2 frost, causing a significant decrease of the pumping speed. Dawbarn was the first to suggest a possible mechanism for the sorption of H_2 by cryodeposits; but he did not attempt to formulate a mathematical model. His ideas were based largely on the data given in Fig. 2.

"...the sorption process might be considered in two parts:

1. Impingement of H_2 molecules at the surface of the cryodeposit results in surface capture. For a fixed quantity of H_2 added to the system, one would thus expect an equilibrium to be established, where for a specific concentration of H_2 molecules within this surface, the reevaporation rate would match the condensation rate. At this point the pumping would stop. However, coupled with this process there is:

2. A diffusion of H_2 molecules within the cryodeposit matrix from the region of high concentration at the surface. The rate constant for this diffusion is evidently strongly dependent upon the cryodeposit temperature."

In parallel with Dawbarn's studies, Busol and Yuferov were investigating cryosorption of H_2 with a variety of frosts (CO_2, H_2O, N_2, Ar, alcohol, benzene, and acetone) in Russia (Refs. 4 and 6). Their experimental apparatus was very similar to that of Dawbarn, but they formed the cryodeposits in an importantly different way. They reported that the frost layer was always formed at about 20°K after filling the sphere with liquid hydrogen (LH_2), and then the temperature of the sphere and frost were reduced to 16 or 14°K by lowering the pressure of the boiling H_2, and hence supercooling it.

The main and new contribution of Busol and Yuferov to the knowledge of cryosorption properties of frost was their measurement of the equilibrium isosteres and isotherms[3] for H_2 sorption by CO_2 and other frosts. For experimental convenience, these investigators measured the sorption isosteres which are given in Fig. 3. These data were cross-plotted to produce the isotherms shown in Fig. 4. It should be noted that these isotherms represent frosts at various temperatures but formed at a temperature of 20°K. The significance of the isotherms or isosteres is that they specify the maximum sorption capacity that can be expected from a sorbent at given chamber pressures and frost temperature. Also, for equilibrium systems the isostere data (Fig. 3) may be used with the Clapeyron-Clausius equation to determine the heats of sorption. Busol and Yuferov reported that the heat of sorption of H_2 on CO_2 frost varies from 800 to 1400 cal/mole. Because the measured heat of sorption is far less than typical heats of chemisorption, Busol and Yuferov concluded that the sorption process is physical in nature.

It was also found that capacity of the frost depended upon its volume in agreement with Dawbarn and that the H_2 penetrated rapidly into the CO_2 frost. They also reported that N_2 and Ar exhibited very poor sorption capacity for H_2. As a result, they speculated that the frost had many finely divided pores of atomic dimension and that more complex polyatomic molecules have greater sorption capacity. At one point they suggest that "only carbon-containing substances have an effective pumping action." Carbon dioxide frost possessed the best capacity of all the cryodeposits they examined,

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[3]The amount of gas, c, at a given temperature adsorbed or sorbed by a substance under equilibrium conditions may be empirically expressed by a function:

$$c = f(P,T)$$

One may experimentally measure the amount of gas sorbed at various chamber pressures by a constant temperature sorbent and hence define an isotherm as

$$c = f(P) \text{ for } T_{sorbent} = \text{constant}$$

Alternatively, one may define an isostere as

$$P = f(T) \text{ for } c_{sorbed} = \text{constant}$$

Plots of these functions are widely used to generalize gas adsorption data.

and the maximum capacities they reported (Fig. 4) for CO_2 at 14°K are significantly greater than those reported by Hunt, et al. (Fig. 1). They also observed that the presence of N_2 reduced the pumping speed and capacity of CO_2 frost, as had Dawbarn.

In addition to measuring sorption isotherms and showing that frost sorption is a physical sorption process, Busol and Yuferov were the first investigators to point out the importance of the frost structure and speculate about the role it played. They did not propose a complete sorption mechanism but concluded that CO_2 frost possessed a "more open" structure.

The only other reported study of the cryosorption of H_2 by cryodeposits is a brief paper by Müller at the Technische Universtat, Dresden (Ref. 7) which presents some isotherm data for H_2 sorption on CO_2 frost. Müller measured a heat of adsorption of about 900 cal/mole, which agrees very well with the values obtained by Busol and Yuferov. He also notes that solid N_2, Ar, and methane (CH_4) sorbents were ineffective for sorption of H_2 as well as for neon (Ne) and He.

For reference purposes, a few isotherms describing the sorption of He on frosts at temperatures of 4.2°K and below are given in Figs. 5 and 6. These data are reproduced from the references given on the figures.

Finally, it should be noted that Hemstreet, et al. (Ref. 18), as well as other investigators, simultaneously added H_2 with a relatively large amount of another gas (N_2, CF_4 (tetrafluoromethane), CH_4, $CClF_3$ (chlorotrifluoromethane or Freon® 13), $CHClF_3$ (chlorotrifluoromethane), CCl_2F_2 (dichlorodifluoromethane or Freon 12), and CO_2) in a chamber which contained a 20°K cryosurface. They detected various degrees of H_2 pumping and attributed it to trapping by the condensable gas. They stated that CO_2 was the best "trapping media."[4] It is believed by this author, however, that the phenomenon they observed was the frost cryosorption phenomenon detected by Hunt, et al., Southerlan, Dawbarn, and Busol and Yuferov, rather than what they referred to as trapping. The amount of H_2 that Hemstreet, et al. could continuously pump while simultaneously adding CO_2 is reasonably consistent with the isotherm data of Busol and Yuferov. In any case, these investigators were the first to show that the sorbent may be formed continuously and need not be predeposited.

Taken in total, all of the investigations of cryosorption of H_2 by cryodeposits are consistent in that they show that frosts can be an effective sorption-pumping medium. Several of the investigators found that the sorption effectiveness of the cryodeposits is quite sensitive to the temperature of the frost, but the exact dependence and reasons are not known. All of these studies indicated that the sorption effectiveness depended largely on the specie of the frost. Perhaps fifteen different types of frost have been tried as a sorbent for H_2 in one way or another. All of the studies agreed that, of the types tried, CO_2 is the most effective; but reasons why this is so are unknown.

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[4]The authors of Ref. 18 refer to cryotrapping as the process of burying and physically trapping noncondensable gases in the solid structure of the condensables formed during conventional cryopumping.

Because of the large number of variables involved, the differences in the experiments themselves, and the different ways the pumping speed was computed, it is difficult to make meaningful comparisons between investigations. However, when the differences in the factors which have been shown to influence the pumping speed and/or capacity of the frost (i.e., frost temperature, frost specie, sorbate gas temperature) are taken into account, there are still significant inexplicable differences between the various investigations. As an example, data from four investigations of the sorption of 300°K H_2 by CO_2 frost are summarized in Fig. 7. The pumping speeds vary between about 20 and 30 liters/sec-cm^2, but the maximum capacities of the frost vary by almost an order of magnitude. The variation of capacity measured by the various investigators cannot be attributed solely to the different frost temperatures. Similar discrepancies exist in the available isotherm data. Also, it has been shown both with the sorption of H_2 and He that the pumping speed and sorption capacity can be significantly reduced if certain other gases are present in the chamber. Clearly, other factors which are as yet undefined must be influencing the cryosorption effectiveness of frosts.

With this as a starting point, an experimental test program was undertaken to attempt to resolve many of the differences in the existing data, as well as to provide information which might lead to a better understanding of the entire process. Because it was felt that the frost structure was the key to putting the entire pumping process into perspective, formation of the frost sorbents was more carefully controlled and documented than had been done by previous investigators. The test apparatus, instrumentation, and procedures used during this program are described in Section III.

SECTION III
EXPERIMENTAL APPARATUS AND CALIBRATIONS

3.1 CHAMBER AND PUMPING SYSTEM

The 36-in.-high by 30-in.-diam stainless steel vacuum chamber used for cryosorption of H_2 is schematically shown in Fig. 8. Its pumping system consisted of a mechanical roughing pump and a 6-in. oil diffusion pump which was equipped with a liquid-nitrogen (LN_2)-cooled baffle, and had a pumping speed of 1500 liters/sec. A 6-in., high-vacuum, air-operated gate valve was used to isolate the chamber from the pumping system. Access to the chamber is achieved by means of a removable top which employed an O-ring seal. The chamber base pressure without bakeout was between 5×10^{-7} and 1×10^{-7} torr.

A 25-in.-high by 24-in.-diam stainless steel shroud was installed in the chamber. It was constructed from overlapping slats (see Fig. 8) in a manner to allow free passage of the molecules, but was optically tight. The shroud was maintained at room temperature for all of the H_2 sorption tests. The cryosorption pump was centrally located inside the shroud, and, together with the shroud, was attached to the removable chamber top. After correcting for the space occupied by the shroud, sorption pump, and other items, the chamber had a free volume of 300 liters.

3.2 CRYOSORPTION PUMP

The cryosurface upon which the frost sorbent was deposited was a simple 6-in.-diam stainless steel sphere with an available pumping area of 970 cm^2 as shown in Fig. 8. It was attached to a vacuum-jacketed concentric GHe supply and return line which was installed in the removable lid. This concentric line was in turn plumbed directly to an He refrigerator via vacuum-jacketed transfer lines. The refrigerator was a modified Collins cryostat which had about 180 w of refrigeration capacity and supplied GHe in the temperature range from 12 to 70°K.

3.3 GAS ADDITION SYSTEM

Hydrogen, as well as the various gases predeposited to form the sorbents were obtained from commercially available high-pressure bottles. These gases were introduced into the top of the chamber in the region between the shroud and chamber wall by means of two gas addition systems. Generally, one system was used to add the sorbent gas and the other to add H_2. Both systems, schematically shown in Fig. 9, consisted of a reservoir or surge tank, a pressure measuring device, several sintered steel leaks arranged in parallel, and an independent vacuum system.

It was not possible to measure directly either the sorbent thickness or its uniformity. However, since the gas molecules would have to have many collisions with the chamber walls and baffles before they could pass through the optically tight shroud, it is believed that the molecules struck the pumping surface randomly from every direction. As a check, however, both the sorbent gas and H_2 were introduced sequentially into the chamber at the same point, for some of the tests. Thus, if the particle ballistics were such that more sorbent was deposited in one place than another, then the H_2 would also strike at a higher rate in these same regions. However, the test results appear unaffected by the gas addition location. After the sorbent had been added on the pumping surface at temperatures below 20°K and before the H_2 addition was started, the base pressure decreased to about 1 to 4 x 10^{-8} torr.

3.4 INSTRUMENTATION

An ion gage and a magnetic-deflection-type mass spectrometer were used to measure the pressures in the chamber (see Fig. 8). Tubulation inside the chamber was employed to prevent the gages from directly sensing the pumping surface, and oriented so that the gages would sense about the same flux of particles as the pumping surface. The time constant of the tubulation has been calculated to be 3.8 x 10^{-6} sec for 300°K H_2 (Ref. 5). For higher pressure tests, the ion gage was replaced with an Alphatron®. Ion gage and mass spectrometer outputs were recorded on strip charts with time as a variable. The pressure on the high-pressure side of the porous plug leaks in the gas addition system was monitored with a conventional bellows-type gage, and recorded by means of a transducer and a strip chart recorder.

An H_2 vapor-pressure thermometer was used to determine the temperature of the GHe-cooled surfaces at temperatures between 10 and 25°K. At higher temperatures an He

gas thermometer was employed. The bulbs of both of these devices were located inside of the sorption pump and heliarc welded into holes in the pumping surface. Iron oxide was used in the bulb of the H_2 vapor thermometer as a catalyst to promote conversion to parahydrogen.

3.5 GAS ADDITION LEAK CALIBRATION

If two volumes at pressure levels of P_a and P_c are connected by a small leak with a conductance K, then the resulting throughput, $\dot{Q}$, may be expressed by,

$$\dot{Q} = V_a \frac{dP_a}{dt} = K (P_a - P_c)$$

When $P_c << P_a$ this equation may be easily integrated, yielding

$$\ell n\, P_a = \frac{\dot{K}t}{V_a} + \ell n\, C_i$$

For some initial value of $P_a = P_i$ at $t = 0$, this equation may be solved for the conductance of the leak, resulting in

$$\dot{K} = \frac{V_a}{t} \ell n \frac{P_a}{P_i} \tag{1}$$

By utilizing Eq. (1), each leak was calibrated for each of the gases used by recording the forepressure decay in the gas addition system as gas flowed through the leak into the evacuated chamber. The volume of the gas addition system upstream of the porous plug leak, V_a, had previously been measured by filling the system with alcohol and measuring its volume (Ref. 5). The calibrations were carried out several times during the course of the tests. The variation of the leak conductances during these calibrations was within ±5 percent.

3.6 ION GAGE AND MASS SPECTROMETER CALIBRATION

The sensitivity, a, of an ion gage or mass spectrometer is defined by

$$P = aP^*$$

where P^* is the gage reading. All pressure gages were calibrated in place to determine their sensitivity for H_2. The calibration technique is described below.

As gas is introduced into a vacuum chamber which is isolated from its pumping system, the chamber pressure increases because of the addition, as well as because of chamber outgassing and leakage. For a constant volume chamber, the rate of pressure increase may be written as

$$\frac{dP}{dt} = \frac{\dot{Q}_{add} + \dot{Q}_o}{V_c}$$

where $\dot{Q}_{add}$ is the throughput being added to the chamber and $\dot{Q}_o$ is an equivalent throughput attributed to outgassing, leakage, etc. The amount of gas added through a calibrated leak is given by

$$\dot{Q}_{add} = P_a K$$

The outgassing and inleakage gas load may be expressed by

$$\dot{Q}_o = V_c \left[\frac{dP}{dt}\right]_o$$

where $(dP/dt)_o$ is the rate of pressure increase in an isolated chamber attributed to outgassing and leakage alone. These equations can be combined to obtain the following expression for the pressure gage sensitivity, assuming that α is independent of time for short times.

$$\alpha = \frac{P_a K}{V_c \left\{\frac{dP^*}{dt} - \left[\frac{dP^*}{dt}\right]_o\right\}} \tag{2}$$

Equation (2) illustrates that dP^*/dt versus P_a plots should yield straight lines, the slope of which are proportional to the gage sensitivity, and can be used to determine the ion gage and mass spectrometer sensitivities in the following manner.

After the chamber was pumped to its ultimate pressure level by means of the diffusion pump, it was then valved-off from the pumping system. As the pressure in the chamber rose because of outgassing and leakage, the ion gage and mass spectrometer readings were recorded continuously on a strip chart to obtain $[dP^*/dt]_o$. Then, the chamber was again evacuated and the valve closed. Next, H_2 was bled into the chamber through a previously calibrated sintered steel leak at a given forepressure, P_a, and the ion gage and mass spectrometer readings recorded continuously to obtain dP^*/dt. This procedure was repeated for several forepressures. It was found that the ion gage sensitivity exhibited a characteristic long-term decrease apparently because of contamination effects. Consequently, all of the pressure instrumentation was calibrated before each series of tests. The gage sensitivities did not change with sufficient rapidity to require calibration before each individual test run.

3.7 VAPOR AND GAS THERMOMETER CALIBRATIONS

An H_2 vapor pressure thermometer was employed to measure temperatures from 10 to 25°K. The H_2 vapor pressure was measured with a 0- to 100-psia gage having a low internal volume and used to obtain temperatures from the parahydrogen vapor pressure curve shown in Fig. 10a. The thermometer had previously been calibrated at 20.4°K by submerging the bulb in LH_2 at atmospheric pressure. The supply and return temperatures of the cold He supplied to pumping surfaces were also measured with factory-calibrated GHe thermometers installed in the cryostat. As shown in Fig. 10b, temperatures measured with the H_2 vapor thermometer were quite close to the arithmetic mean

temperature of the refrigerated He in the supply and return lines. It is assumed that the surface temperature of the frost is closely approximated by the bulb temperature. Temperatures obtained with the H_2 vapor thermometer are believed to be accurate to ±0.5°K in the range between 12 and 25°K.

For tests during which the sorbent was warmed above 25°K, an He gas thermometer was used. It was calibrated against the H_2 vapor pressure thermometer in the range from 12 to 25°K. This calibration curve (Fig. 11) was extrapolated to higher temperatures as guided by the mean temperature in the GHe supply and return lines. Temperatures between 25 and 40°K are believed to be accurate within ±2°K. Above 40°K, measured temperatures are believed to be accurate to within ±5°K.

SECTION IV
PROCEDURES

Before each series of sorption pumping runs, the molecular leak and pressure gage calibrations were carried out by the methods described in the preceding section. All runs were started by pumping the chamber to its base pressure level by the diffusion pump.. The two gas addition systems were evacuated by their pumping systems and flushed several times with the gas to be used.

Next, the cryosurface was cooled by circulating cold GHe from the cryostat through it. Its temperature was monitored by the H_2 vapor thermometer and the supply and return temperatures at the refrigerator. At the maximum refrigerator capacity, the cryosurface could be maintained at 12°K. By bypassing a portion of the cold He, the cryosurface temperature could then be adjusted to the desired temperature. When this temperature was reached, the chamber was isolated from its pumping system and ready for admission of the sorbent gas.

4.1 FORMATION OF SORBENT FROST

All of these tests were conducted by predepositing the frost sorbent before beginning the addition of H_2. The sorbent gases used for these tests and their purities as given by the manufacturer (Matheson Chemical Co.) are listed in the following table:

Sorbent	Purity, percent
CO_2	99.99
SO_2 (Sulphur Dioxide)	99.90
CH_3Cl (Methyl Chloride)	99.50

The reservoir of the sorbent gas addition system was filled to a particular forepressure which established the sorbent addition rate. As the sorbent gas was admitted into the isolated chamber, the pressure rose to a level which depended upon the forepressure. Some typical values of the chamber pressure at which the sorbent was formed, the sorbent strike rate, and the approximate growth rate of the frost are summarized below for the CO_2 sorbent at various forepressures.

TABLE I
FROST FORMATION CONDITIONS

Chamber Pressure, torr	CO_2 Strike Rate, molecules/cm^2-sec	$d\bar{\ell}_f/dt$, μ/min
2×10^{-6}	6.3×10^{14}	0.0045
2×10^{-5}	6.3×10^{15}	0.045
2×10^{-4}	6.3×10^{16}	0.45
1×10^{-3}	3.15×10^{17}	1.0

Most of the sorbents were formed at different pressure levels or strike rates by varying the leak forepressure. However, a few were formed by pumping the chamber to its base pressure and then backfilling it with He to pressures as high as 10^{-1} torr. The sorbent gas was then introduced into the chamber and the sorbent formed at relatively high He partial pressure levels. Both the leak forepressure and chamber pressures were recorded continuously and held constant during the prescribed addition time. Then the He was removed from the chamber by the diffusion pump.

The forepressure, together with the leak calibration, allowed measurement of the amount of sorbent added, $\dot{Q}_s$. For convenience of discussion, the mean thickness of the sorbent frost was estimated from $\dot{Q}_s$, assuming that all of the sorbent gas added to the chamber was deposited on the cryosurface.

$$\dot{m}_s = \frac{\dot{Q}_s M}{k T_g} = \dot{m}_f = \rho_f A_f \bar{\ell}_f$$

or

$$\bar{\ell}_f = \frac{M \dot{Q}_s}{A_f \rho_f k T_g} \tag{3}$$

The density of the frost is needed to estimate the frost thickness. Densities of some species of frost used for these tests are available, but the densities of others had to be estimated from the published values of their liquid density and the general trends between liquid and frost densities. It is of interest to note that, for the substances where measurements are available (CO_2, H_2O, N_2, and Ar), the densities of cryodeposits formed directly from the gas phase are about 10 to 20 percent lower than the densities of solidified gases formed from the liquid phase. This suggests that the crystal structure of cryodeposits may be less ordered.

Sorbent	ρ_{liq}, gm/cm^3	ρ_f, gm/cm^3	Reference
CO_2	1.19	1.60	Ref. 19
N_2	0.80	0.90	Ref. 20
Ar	1.41	1.77	Ref. 21
SO_2	1.46	1.80	Estimated
CH_3Cl	1.00	1.20	Estimated

Sorbent thicknesses from 0.1 to 4 μ were achieved by varying the flow rate and time of the sorbent addition.

4.2 KINETIC PUMPING MEASUREMENTS

Once the frost was deposited, the sorbate gas was admitted to the chamber through its gas addition system; the chamber remained valved-off from its pumping system. The leak forepressure was held constant during the addition to maintain the sorbate addition rate constant at some desired value. Typical time histories of the chamber pressure and sorbate forepressure for this mode of operation are given in Fig. 12. Preliminary tests demonstrated that, when the chamber pressure had increased to about 3×10^{-4} torr, the frost sorbent was essentially saturated[5] with the sorbate and its pumping speed was reduced to a few liters/sec. The test runs were terminated at this point by shutting off the sorbate flow.

4.3 ADSORPTION ISOTHERM MEASUREMENTS

Equilibrium adsorption isotherm data were obtained by predepositing the sorbent and introducing the H_2 sorbate at a constant rate. However, the H_2 flow was periodically interrupted and the chamber pressure allowed to reach its equilibrium value. After this occurred, the sorbate flow was again initiated. This process was repeated several times until the frost became saturated; that is, the saturation pressure was reached. A typical chamber pressure history during an adsorption isotherm test is given by Fig. 13.

4.4 DESORPTION ISOTHERM MEASUREMENTS

Figures 4, 5, and 6 indicate that, after the frost is saturated, it is possible to desorb some of the sorbate by decreasing the chamber pressure. This provides the basis for the measurement of equilibrium desorption isotherms. When the frost was completely saturated and the sorbate flow terminated, the diffusion pump was employed to decrease the chamber pressure to some predetermined level. Inasmuch as the pumping speed of the diffusion pump for H_2 had been previously measured, it was possible to estimate the amount of gas desorbed by a numerical integration of

$$Q_{desorb} = \int_0^{t_o} S\, P(t)\, dt$$

where P(t) is the measured pressure variation with time when the valve to the diffusion pump was opened. Then, the chamber was valved-off and allowed to reach equilibrium. Next, the sorbate gas flow was again started. The amount of sorbate gas needed to saturate the frost and restore the chamber pressure to the original saturation pressure was measured (see Fig. 14) and found to be in good agreement with the estimates of the amount of gas desorbed. This process was repeated for different pressure levels to define equilibrium isotherms for the desorption process.

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[5]Definition of the saturation point of the frost is somewhat arbitrary, but it is taken here as the point where the chamber pressure reaches 3×10^{-4} torr, which is referred to hereafter as the saturation point.

4.5 DESORPTION BY WARMING THE SORBENT

Isotherms measured at various sorbent temperatures (Figs. 4 and 6, for example) illustrate that the sorbed gas would also be desorbed if the frost temperature is increased. This was achieved through bypassing some of the cold He in the cryostat, thus increasing the cryosurface temperature. As He was bypassed, the chamber valve was opened so that the diffusion pump could remove the desorbed sorbate, and the cryosurface temperature was monitored with the gas and vapor thermometers. When the desired warmup temperature was achieved, the bypass valve was closed and the cryosurface temperature again decreased to the desired value in preparation for another sorption test.

4.6 CALCULATION OF FROST SORPTION CAPACITY

The amount of gas pumped by a frost sorbent or a molecular sieve has also been reported in a variety of ways. A nondimensional method is employed here.

The amount of gas added to the chamber to form the sorbent was computed from

$$Q_{sorbent} = t\,[P_a K]_{sorbent}$$

where Q has, as convenient dimensions, torr-liters. When the sorbate was added at a constant rate, a similar calculation was made for it.

$$[Q_{sorbate}]_{P_a} = t[P_a K]_{sorbate}$$

The sorption capacity of the frost was then defined as

$$C \equiv \frac{[Q]_{sorbate}}{[Q]_{sorbent}}$$

The quantity C is referred to as the "mole ratio" by some investigators (Refs. 5, 8, and 9), and as the "concentration" by others (Refs. 4, 6, and 10). It is merely a convenient nondimensional way to express the amount of gas which has been sorbed and is referred to here as the capacity of the frost. It also describes how many molecules may be sorbed by each molecule predeposited in the frost. The value of C at the saturation pressure is referred to as the saturation capacity.

The volume of gas sorbed in cubic centimeters divided by the mass of the sorbent in grams is also quite frequently used in the isotherm and molecular sieve literature (Ref. 7) to describe the quantity of gas sorbed by a porous medium. This parameter is analogous to the factor C employed here.

SECTION V
RESULTS AND DISCUSSION

5.1 ISOTHERM MEASUREMENTS

5.1.1 Sorption Isotherms

The variation of the test chamber pressure which occurred as 300°K H_2 was continuously being sorbed by a 1-μ-thick layer of CO_2 cryodeposit at 12.4°K is shown by the dashed line in Fig. 15a. Because a constant sorbate addition rate was used, this figure also represents a typical chamber pressure history as a constant H_2 gas load is being pumped. If the sorbate flow was stopped, the chamber pressure would decrease to the lower equilibrium values shown by the symbols. These points define then the equilibrium sorption isotherm for a 12.4°K CO_2 cryodeposit, which was formed at a strike rate of 6.15×10^{15} mole/cm^2-sec. Data obtained at the lower values of capacity are not presented because the measured pressures are governed by the chamber inleakage and outgassing and do not define the isotherm. The true isotherm, at lower pressures, would approximately follow the short dashed line extrapolation. The sorbate flow was always finally stopped at a pressure level corresponding to point c, the saturation pressure where the frost was fully saturated for all practical purposes.

Comparing the actual operating pressure curve to the equilibrium isotherm illustrates that cryosorption pumping on frost is far from an equilibrium process during the initial stages of pumping. As the saturation pressure is approached (point c), the two curves are essentially coincident.

5.1.2 Desorption Isotherms

After the saturation pressure was reached via path abc in Fig. 15a, the sorbed H_2 could be desorbed from the frost by opening the valve to the diffusion pump and lowering the chamber pressure to some value, for example, as given by point b in Fig. 15b. The amount of H_2 sorbate then needed to again saturate the frost corresponded to the change in capacity between b and c. Equilibrium desorption isotherms were obtained by repeating this process at various pressures, a typical example of which is given by the solid line in Fig. 15b. Comparison of the sorption and desorption isotherms in Figs. 15a and b shows that they are essentially identical. Desorption isotherms for cryosorption on frosts have not been published previously.

During the desorption process, the pressure could be reduced in a few minutes to about point e in Fig. 15b with the available diffusion pump. At this point an equilibrium between frost adsorption and desorption and chamber outgassing and pumping was established, and continued pumping for several hours did not produce a significant decrease in pressure. Thus, it was not possible to completely desorb the H_2 from the frost. However, these tests demonstrated that CO_2 frost can with intermediate desorption

be used over and over to pump H_2. If this desorption method is employed, the reuse capacity of a frost for subsequent cryosorption pumping would be only roughly a third of its initial capacity for the present test apparatus. In view of subsequent tests, this residue capacity, however, may be fixed by the nature of the frost structure. This point will be discussed in more detail later.

5.1.3 Comparison with Other Investigations

Measured equilibrium isotherms for the sorption of H_2 by CO_2 frost at temperatures of 12.4, 16.5, and 21.5°K are summarized in Fig. 16, together with isotherm data available from other investigations. For these tests, frosts were formed at the same temperature at which the subsequent cryosorption pumping took place and at a strike rate of 6.15×10^{15} molecules/cm^2-sec. Additional isotherm measurements were made in which the frost was formed in the same fashion but at different thicknesses (up to 4 μ) and allowed to "age" for several hours before the cryosorption test was begun. Increasing the frost thickness, of course, allows a greater amount of H_2 to be sorbed; but on the dimensionless basis of capacity, different thickness frosts produced the same isotherms. Allowing the frosts to age did not alter their isotherms. Thus, it is believed that no long-term reorientation of the frost structure occurs after it is deposited.

It is generally stated that the adsorption and desorption energies are approximately the same, although only a few measurements are reported in the literature (see Ref. 22, Fig. 9-2, for example). Because the sorption and desorption isotherms for frost are coincident, it follows that the sorption and desorption energies for this sorbent-sorbate system must be equal. The present test results agree with those reported by Yuferov and Busol (Ref. 6) and correspond to a heat of sorption or desorption of about 1200 cal/mole.

The present isotherm data appear to agree with those published previously by Yuferov and Busol (Ref. 6), but it will be seen later that this result is fortuitous. Frosts used in the present tests, however, exhibited considerably higher saturation capacities than those investigated by Dawbarn (Ref. 5) and Müller (Ref. 7), as well as higher capacities than those studied by Hunt, et al. (Ref. 2), and Southerlan (Ref. 3). These latter data are not shown in Fig. 16 because Hunt and Southerlan did not report the equilibrium chamber pressure at saturation. The reasons for these differences were not immediately evident, but were subsequently attributed to differences in the frost structure.

5.2 THE FROST STRUCTURE

5.2.1 The Known Structure of Solid Carbon Dioxide

When formed from the liquid state, CO_2 crystals are face-centered cubics with a lattice constant of a_o = 5.575 Å at 83°K (Ref. 23). The temperature dependence of its lattice constant is given by the empirical equation

$$a_o = 5.54 - 4.679 \times 10^{-6} T^2$$

where T is in °K. So, in the temperature range of this study, the lattice constant would have a value of about 5.54 Å. Additional information concerning the structural defects of solid CO_2 formed from a liquid are contained in a paper by Coucoulos and Gregory (Ref. 24). These investigators reported that, at atmospheric pressure, solid CO_2 at a temperature of 77°K has a polycrystalline structure and the voids are filled with CO_2 gas. Also, as the solid is allowed to warm to room temperature, they reported that it undergoes various structural changes.

Very little is known about the structure of CO_2 cryodeposits, but the generally held speculation is that solidified gases in the form of cryodeposits are amorphous. Graf and Paulon (Ref. 25) have reported the results of two X-ray diffraction measurements indicating the structure of CO_2 cryodeposit formed on a surface at about 80°K. When the deposit was formed at a pressure level of about 4 x 10^{-3} torr by directing a CO_2 jet on the cryosurface, the diffraction patterns show that the cryodeposit possessed a definite cubic structure. However, when the cryodeposit was formed at a higher pressure of 10^{-1} torr, no diffraction patterns existed. These investigators believed that the deposit formed at the higher pressure was amorphous, while the one formed at 4 x 10^{-3} torr was polycrystalline. Also, they believed the structure of the deposit was influenced by the manner in which they directed the CO_2 onto the cryosurface.

5.2.2 Effect of Frost Temperature on Its Structure

At pressure levels of about 10^{-7} torr, CO_2 will begin to condense on a surface when its temperature is decreased to about 80°K.[6] If a cryodeposit is formed at this temperature or just below, one would expect the surface-captured molecules to be rather mobile. They may migrate over the surface until they find positions of minimum potential energy with respect to other captured molecules which would correspond to lattice positions in some crystalline state. However, if the cryosurface temperature is well below that required for condensation, the captured molecules would be much less energetic after capture. As a result, they may not move very far from their random adsorption sites before being covered by other captured molecules which strike the surface at random positions. Consequently, forming a cryodeposit on a surface at well below the condensation temperature should tend to produce a more disordered amorphous-like structure, while forming a deposit at near the condensation temperature would be in the direction to produce a more crystalline-like structure. Carbon dioxide cryodeposits used in this and other cryosorption investigations were formed at temperatures between about 12 and 20°K, which is considerably below the condensation temperature of about 80°K. As a result, they would be expected to be more disordered than the frost structures examined by Graf and Paulon, for example.

Previous investigators have observed that sorbed H_2 may be quite effectively desorbed by increasing the frost temperature. The isotherms (Fig. 16) show that a CO_2 frost warmed to 20°K would contain only a small amount of residual H_2. Consequently,

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[6]This corresponds to a temperature slightly lower than specified by the vapor-pressure curve at $P = 10^{-7}$ torr. For convenience, we will refer to the condensation temperature of any gas as a temperature slightly lower than that for a vapor pressure of 10^{-7} torr.

warming the frost would appear to provide a better means of desorbing it than lowering the chamber pressure. However, the effect on its structure of raising the frost temperature must be considered.

When a cryodeposit is warmed to a higher temperature, then its molecules become more mobile, and they tend to reorientate themselves toward a more orderly polycrystalline or crystalline state. Cooling the frost back to its original temperature would not restore the original more disordered structure, because decreasing the frost temperature decreases the molecular mobility. This would have the effect of locking the more ordered structure, corresponding to the higher temperature, in place. Similarly, if a cryodeposit formed at one temperature is subsequently cooled to a lower temperature, it should retain the type of structure characteristic to the higher initial temperature. These ideas were proposed a few years ago by Hemstreet, et al. (Ref. 18) to explain some of their cryotrapping results.

The effect on sorption capacity of warming a frost to some higher intervening temperature is shown in an interesting series of equilibrium isotherms in Fig. 17. In all cases except one, the frosts were initially formed at the temperature at which the isotherms were measured—12.4, 16.5, or 21.5°K—and at a strike rate of 6.3 x 10^{15} mole/cm^2-sec. After the frost was saturated with H_2, its temperature was increased and the desorbed H_2 removed from the chamber by the diffusion pump. Then, the frosts were cooled again to their initial temperatures and resaturated. Inspection of the isotherms in Fig. 16 shows that a saturated 12.4°K frost when warmed to 20°K would retain a slight amount of residual H_2 (corresponding to a capacity of about 0.005 at a pressure level of 10^{-7} torr). If there were no changes in the frost's sorption properties caused by warming, the subsequent saturation capacity of the desorbed frost would be only slightly less than its initial saturation capacity. Isotherm data in Fig. 17 indicate that this is not the case. For example, Fig. 17a shows that warming a 12.4°K CO_2 frost to 20°K and recooling it to 12.4°K resulted in reductions in the subsequent sorption capacity which were several times larger than expected from Fig. 16. Furthermore, it is evident by inspection of the remaining isotherms in Fig. 17a that the higher the temperature used to desorb the frost, the greater the loss in subsequent saturation sorption capacity. For example, when the frost was warmed to 60°K and then cooled back down to 12.4°K, its saturation capacity was only 20 percent of the original value. Although fewer data were obtained, the reuse capacities of 16.5 and 21.5°K CO_2 frosts were also significantly reduced when they were warmed to intervening temperatures of about 40°K (see Figs. 17b and c, respectively). These reductions in the sorption capacity are not caused by partial desorption as occurred when the frost was desorbed by lowering the chamber pressure, but rather it is believed that they reflect the change in the frost structure as it is warmed and the varying capacities of different types of frost structures to sorb a gas.

An equilibrium isotherm for a CO_2 frost which was deposited at a temperature of 22°K and then cooled to 12.4°K is also contained in Fig. 17a. It is of interest to compare it to the isotherm for a frost deposited at 12.4°K, and saturated with H_2,

warmed to 20°K to desorb the H_2[7], and then recooled to 12.4°K. The frost formed at 22°K has a somewhat lower capacity; thus it would appear that frost formed at some higher temperature may be somewhat more ordered than frosts which are warmed to that temperature. In any case, it is apparent that the frost capacity is strongly dependent upon the maximum temperature which it has experienced. There appear to be no significant differences in the capacity of frosts which are deposited at some temperature or warmed to that temperature after they were deposited at a lower temperature.

Hengevoss (Ref. 26) has recently reported somewhat similar findings for a limited number of tests of the sorption of H_2 at a temperature of 77°K by multimolecular layers of condensed Ar. His results, although quite sketchy, also imply that sorption effectiveness of Ar frost depends upon its temperature history. He also found that an Ar frost formed at 20°K and then cooled to 9°K possessed a somewhat lower capacity than one formed at 9°K, warmed to 20°K, and cooled again to 9°K.

In addition, a brief review of some actual operating experience with frost cryosorption pumping may be instructive at this point. Independent of this study, a CO_2 cryosorption pump has been employed to pump H_2 in a molecular beam chamber at AEDC. Upon occasion, the CO_2 frost would exhibit extremely low sorption capacities for no apparent reason. A subsequent review of the operating procedures, however, revealed that the CO_2 frost was often deposited as the cryosurface was being cooled and began as soon as the temperature reached about 80°K. In light of the more recent information provided by this investigation (Fig. 17), the reason for the attendant low capacity of cryosorption frosts deposited at near their condensation temperatures is apparent.

Figure 17 also illustrates that, even though structural changes take place which decrease its capacity, warming the frost is a superior way to desorb it. It is clear that the frost temperature increase should be as small as possible, consistent with desorbing most of the H_2. Regardless of the cryosorption pumping temperature, there appears to be no advantage to raising the frost temperature above about 20 to 22°K. This will provide a reuse capacity of about 85 to 90 percent of the original value in contrast to the 30 percent reuse capacity when the frost was desorbed by lowering the pressure. Going to higher temperatures would allow the further desorption of a small amount of H_2, but it would result in a lower reuse capacity because of structural changes. As will be seen in a subsequent figure, the frost temperature should never be raised beyond about 30°K.

5.2.3 Effect of Frost Formation Rate on Its Structure

Since the measured isotherms suggested that frosts which were formed in a manner to make them more porous or amorphous or polycrystalline were superior sorbents, additional measurements were made for frosts which were intentionally formed in a manner to make them more disordered. When a cryodeposit is formed at a relatively

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[7]Additional measurements have shown that saturating and desorbing the frost plays no detectable role in the capacity changes. A frost deposited at 12.4°K, warmed to 20°K, cooled to 12.4°K, and then saturated, produced the same isotherm as a frost whose temperature was increased to 20°K to desorb it.

high chamber pressure and hence a high strike rate, the captured molecules would have much less time to wander over the surface in search for lattice positions before being buried by other condensing molecules than if the deposit were formed at a low strike rate. Consequently, forming the frost at high strike rates is in the direction to produce a more disordered or porous-type structure. This idea is consistent with results of the X-ray diffraction measurements of Graf and Paulon of the structure of CO_2 cryodeposits formed at different pressure levels, as mentioned at the beginning of this section.

Equilibrium isotherms for CO_2 frosts formed at different strike rates and chamber pressure levels are given in Figs. 18a, b, and c for temperatures of 12.4, 16.5, and 21.5°K, respectively. They demonstrate that, as expected, frosts formed at higher strike rates have significantly greater sorption capacities. For example, a frost formed at a strike rate of 6.3×10^{16} molecules/cm^2-sec had anywhere from a 35 to 100 percent higher sorption capacity at various chamber pressures than a frost formed at a strike rate of 6.3×10^{15} molecules/cm^2-sec.

As the CO_2 strike rate is increased, there is also an attendant increase of the chamber pressure level at which the cryodeposit is formed and an increase of the actual growth rate of the frost as summarized in Table I. In an attempt to isolate some of these variables, equilibrium isotherms of CO_2 cryodeposits formed in an He background of 1×10^{-1} torr were also obtained and are shown in Fig. 18. In this case, the strike rate of CO_2 molecules and the actual growth rate of the frost were the same as for frosts formed at a pressure of 2×10^{-5} torr. These frosts exhibited still greater sorption capacities. This effect could possibly be attributed to the high strike rate of noncondensable He atoms on the condensing surface retarding surface migration of the captured CO_2 molecules. Another possibility is that buried and trapped He atoms were subsequently desorbed, leaving voids in the structure. In any case, it is apparent that forming the frost in this manner resulted in a more porous structure.

This series of tests demonstrated how the sorption capacity of frosts may be readily improved. Comparison of Figs. 7 and 18 illustrates that H_2 saturation sorption capacities were obtained which were 300 percent greater than achieved during any previous cryosorption investigation. The maximum capacities measured in this investigation indicated that 43 H_2 molecules may be sorbed for each 100 CO_2 molecules in the frost. Further improvements in capacity are undoubtedly possible by forming the cryodeposit at still greater rates; the upper limit could not be determined with the present test apparatus. The gas addition system limited the rate at which CO_2 could be added to the chamber to an equivalent strike rate of 3×10^{17} molecules/cm^2-sec; and, if the chamber was backfilled with He to pressures higher than 1×10^{-1} torr, it was not possible to maintain the cryosurface temperature at 12.4°K because of thermal conduction problems.

Frosts formed at higher strike rates were also subject to a reduction in their subsequent capacity if they were warmed to higher temperatures for desorption purposes (see Fig. 19). This reduction was proportionally greater than that suffered by frosts formed at lower strike rates. This probably occurs because the structure of frosts formed at high strike rates is more disordered. Consequently, they are subject to a larger degree

of reorientation. Their reuse capacity, however, is about 80 to 85 percent of their initial capacities if the frost temperature is not increased above 20°K to desorb the H_2.

A review of some of the gettering experiments (see Refs. 27 and 28), in which H_2 and other gases were chemisorbed on metallic films, has revealed that similar phenomena were observed. Clausing (Ref. 27) found, for example, that titanium films which were formed at a high evaporation rate, or formed in the presence of an inert gas (He or Ar), were superior chemisorbents. He related this improved sorption capacity with a pronounced change in the visual appearance and structure of the deposited metal film. Further, he stated that the better sorbing films were "poorly crystallized" and possessed a greater effective active surface area. Consequently, it is believed that cryodeposits formed at high strike rates or in an inert gas background have superior sorption properties because they are more porous or disordered structures.

5.2.4 Sorption Capacity of Different Sorbent Species

Ten to fifteen different sorbents have been previously investigated, but no one has as yet attempted to explain why some are better sorbents than others. The present tests, although not definitive, do in a general way shed some light on this subject.

The isotherms given in Figs. 17 and 18 consistently demonstrate that frosts which are formed in a way to make them more amorphous or porous have greater sorption capacity. Furthermore, the desirability of depositing the frost at a temperature much below its condensation temperature has been demonstrated. This limits the surface mobility and migration of molecules away from their random adsorption sites which produces more porous deposits. Consequently, the sorption capacity of a frost should be at least roughly related to the difference between the condensation temperature and the temperature at which the cryosorbent is formed. Since cryosorption pumping normally will require frost temperatures between 10 and 20°K, sorbent gases which have condensation temperatures in the range between 20 and 30°K, such as N_2, O_2, Ar, or carbon monoxide, will tend to produce more crystalline-like structures and will inherently be poorer sorbents. Gases which have much higher condensation temperatures such as CO_2 and H_2O should have considerably better sorption capacity if they are deposited at low temperatures (in the 10 to 20° range).

Previous cryosorption investigations which studied several types of sorbents tend to verify this concept (see Figs. 1, 4, and 5). Carbon dioxide and H_2O frosts always exhibited far greater capacities than N_2, O_2, and Ar sorbents. Yuferov and Busol (Refs. 4 and 6) also tried gasoline, alcohol, and other hydrocarbons as sorbents. They did not publish sorption capacity data for these substances but stated that they were far inferior to CO_2. Because they all have high condensation temperatures, this would appear to contradict the proposed importance of the condensation temperature. Thus, a high condensation temperature is a necessary but not completely sufficient condition to high sorption capacity. Two other sorbents which have relatively high condensation temperatures, SO_2 and CH_3Cl, were also examined in this investigation. Both provided interesting results.

Equilibrium isotherms measured while pumping H_2 with an SO_2 frost are summarized in Fig. 20. Its capacity, although somewhat less than that of CO_2 (compare Figs. 17 and 20), is relatively high. Furthermore, where SO_2 frost is warmed to desorb the H_2, its loss in subsequent sorption capacity parallels that exhibited by CO_2 frost. Obviously, as a sorbent, SO_2 is in the same class as CO_2.

Methyl chloride frost, on the other hand, appeared to possess a low sorption capacity. However, when the CH_3Cl sorbent gas was introduced into the chamber, the ion gages and mass spectrometer, tuned to a mass number of 2, indicated a steady pressure increase as shown in Fig. 21. One might attempt to explain the increased mass spectrometer readings in terms of the cracking pattern on CH_3Cl, but this would not explain the higher ion gage readings. Since the cryosurface temperature was about 12°K, it would pump any gas impurities being added to the chamber except H_2, He, or Ne. The latter two gases could not be detected with the mass spectrometer. The only possible conclusion was that H_2 was entering the chamber along with the CH_3Cl. A chemical analysis of the bottled CH_3Cl did not detect the presence of H_2. Consequently, it is believed that the room temperature CH_3Cl may partially decompose when it enters the chamber at a pressure of less than 10^{-7} torr, releasing H_2 which in turn is sorbed by the CH_3Cl (and/or its decomposition products) frost. As a result, the frost was partially saturated with H_2 before the test H_2 was intentionally admitted into the chamber. Thus, its measured sorption capacity was low. If this conclusion is correct, it may explain why some of the previously tried sorbents, such as gasoline, alcohol, acetone, and other complex polyatomic molecules containing H_2, had rather poor sorption capacities. They may also break down at room temperature but at very low pressure. Because this phenomenon was not germane to the main purpose of this investigation, isotherm data for CH_3Cl were not obtained; and it was not studied further.

5.2.5 Explanation of the "Poisoning" Effect of Nitrogen on a Carbon Dioxide Sorbent

Dawbarn (Ref. 5) and Yuferov and Busol (Ref. 6) mention that the presence of N_2 significantly reduced the sorption capacity of CO_2 frost. Dawbarn believed that it acted as a barrier retarding the diffusion of H_2 molecules away from their adsorption sites. The reasons for this behavior now seem clear.

For both of these investigations, N_2 was admitted to the chamber after the CO_2 and was cryopumped on top of the CO_2 frost. Since its condensation temperature is only a few degrees above that of the cryosurface, the N_2 frost layer would tend to be more ordered and inhibit the diffusion of adsorbed molecules into the CO_2. The N_2 frost itself has been shown to be poor sorbent (see Fig. 1), and hence it would act as a surface barrier as Dawbarn proposed. Any other gas, however, which condenses at only a few degrees above that of the cryosorption surface should produce a similar barrier. It is significant to note that N_2 does not provide a barrier to the sorption of He by an Ar frost at 4.2°K, but H_2 does (Ref. 9). Hydrogen will only be captured at temperatures below about 5°K; thus, it must form a well-ordered surface frost layer which retards the diffusion of He.

5.3 SUMMARY AND APPRAISAL OF SORPTION CAPACITY MEASUREMENTS

5.3.1 A Summary View of the Frost Structure

Isotherm measurements presented in this report have resulted in the identification of several factors which influence the sorption capacity and permit the process of cryosorption pumping to be put in better perspective. The maximum H_2 sorption capacities of CO_2 frosts at a temperature of 12.4°K as functions of maximum temperature which the frost has experienced and the pressure at which the frost was formed are presented in Fig. 22. This figure clearly illustrates the advantages of forming the frost at high pressure levels or strike rates and maintaining the frost at low temperature. It also shows that there is no advantage of depositing a frost at a lower temperature than the temperature at which the subsequent cryosorption pumping is to take place. Regardless of the formation strike rate, the reuse capacity of the frost is reduced as its temperature is increased.

These tests consistently suggest that cryodeposits formed at a temperature well below that required to condense the gas and formed at high strike rates have rather disordered or amorphous structures. However, if the frost is formed at low strike rates or at temperatures approaching its condensation temperature, or if the frost is allowed to warm to higher temperatures, a much more ordered or crystalline structure results which has poorer sorption characteristics. Because the more porous frost structures are better sorbents, it follows that the diffusion mechanism must be one of surface diffusion into the pores, cracks, or other defects in the frost. Interstitial or bulk diffusion of the sorbate into an ordered crystal structure is not the predominant diffusion mechanism in frost cryosorption pumping.

Figure 22 also shows an interesting characteristic of CO_2 frost. As the frost temperature was increased above about 30°K, a sudden discontinuity occurred in the sorption capacity. This may indicate the occurrence of a transition in the frost structure, perhaps a large-scale reordering of the frost from an amorphous to some polycrystalline state. After passing through this transition region, it appears that all CO_2 frosts had the same sorption characteristics independent of the conditions at which they were formed. Hence, they all may have changed to the same kind of structure. This phenomenon is the basis for the previous suggestion that, if H_2 is desorbed by warming the frost, its temperature should not be increased above 30°K. Although fewer data were available, the same phenomenon occurs with SO_2 frost. (Compare the maximum capacities for the various isotherms in Fig. 20.) Reference to this behavior could not be found in the available literature describing the properties of solid CO_2.

5.3.2 Explanation of Inconsistencies between Previous Investigations

The results of this investigation now provide the means to explain some of the differences in test results obtained by other investigators. The large variation in the previously measured values of the sorption capacity (Fig. 7) is, in general, because of the different ways in which the frosts were formed by the various investigators. Figure 22 shows that sorption capacity data are only useful and meaningful if they are accompanied

by a description of how the frost was formed and a description of its previous temperature history. This may be illustrated by the following examples:

1. Hunt, et al. (Ref. 2) obtained unexpectedly low capacities (Figs. 1 and 7) for frost temperatures of usually 11°K. This was because they formed the frost at an extremely low strike rate, perhaps two orders of magnitude less than the lowest rate employed in the present investigation. In view of the isotherm data presented in Fig. 18, their low capacity measurements are not surprising.

2. Southerlan (Ref. 3) concluded that H_2O frost at 20.4°K sorbed H_2 better than CO_2 frost at 16°K, and his measured sorption capacities were lower than those obtained by other investigators (Fig. 7). His unusual results stem from the fact that he unwittingly warmed the CO_2 frost to 28°K and then recooled it to 16°K before saturating it with H_2. This procedure may have reduced its capacity by as much as 30 percent (see Fig. 22) and made it appear inferior to H_2O frost when it is actually superior.

3. Yuferov and Busol (Ref. 6) measured isotherms which appear to agree quite well with those of this investigation (Fig. 16). However, they formed all of their frosts at 20.4°K and then cooled them to 14 or 16°K before saturating them with H_2. Figure 22 demonstrates the importance of the temperature history of the frost and illustrates that this agreement is accidental.

4. Müller (Ref. 7) and Dawbarn (Ref. 5) have also presented sorption capacity data for CO_2 frosts. However, since they give no information about how the frosts were formed, there is, in fact, no basis for comparison with the present tests.

SECTION VI
CONCLUSIONS

As a result of these tests, it is now possible to understand the differences in most of the previously published experimental data on cryosorption pumping and to put the cryosorption of H_2 by frosts into clearer perspective.

1. Cryodeposits formed at temperatures much lower than their condensation temperature and/or at high strike rates are basically porous and have considerably higher sorption capactiy than frosts formed at low rates or at a temperature near that specified by its vapor pressure curve.

2. Since a good sorbent must possess a high condensation temperature and its molecules condensed on a cryosurface at as low a temperature as possible, this precludes the use of O_2, N_2, Ar, and other such gases, which are normally cryopumped on 20°K or less surfaces, as cryosorbents for H_2.

3. Sorption capacity or isotherm data for frosts are only meaningful and useful to others if they are documented with the conditions under which the frost was formed and a description of its previous temperature history.

4. Frosts appear to cryosorb gases by the mechanism of surface diffusion into pores, cracks, or other types of defects in the frost structure. Bulk or interstitial diffusion does not play an important role in this cryosorption pumping process.

5. The maximum H_2 sorption capacity achieved during this investigation corresponded to 43 H_2 molecules sorbed for each 100 CO_2 molecules predeposited in the frost. This represented about an order of magnitude increase over that obtained in previous investigations.

6. Sorbed H_2 may be desorbed from the frost by lowering the chamber pressure by some auxiliary pumping means and the frost used again to pump H_2. However, it is not possible to get all of the H_2 out of the frost with this method. The frost may also be warmed to desorb the H_2 but at the consequence of a loss in its subsequent capacity. It appears that, with CO_2 frost, increasing its temperature to between 20 and 22°K and then subsequently cooling it offers about the best compromise in regard to achieving maximum reuse capacity of the frost.

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APPENDIXES
I. ILLUSTRATIONS
II. DEFINITIONS

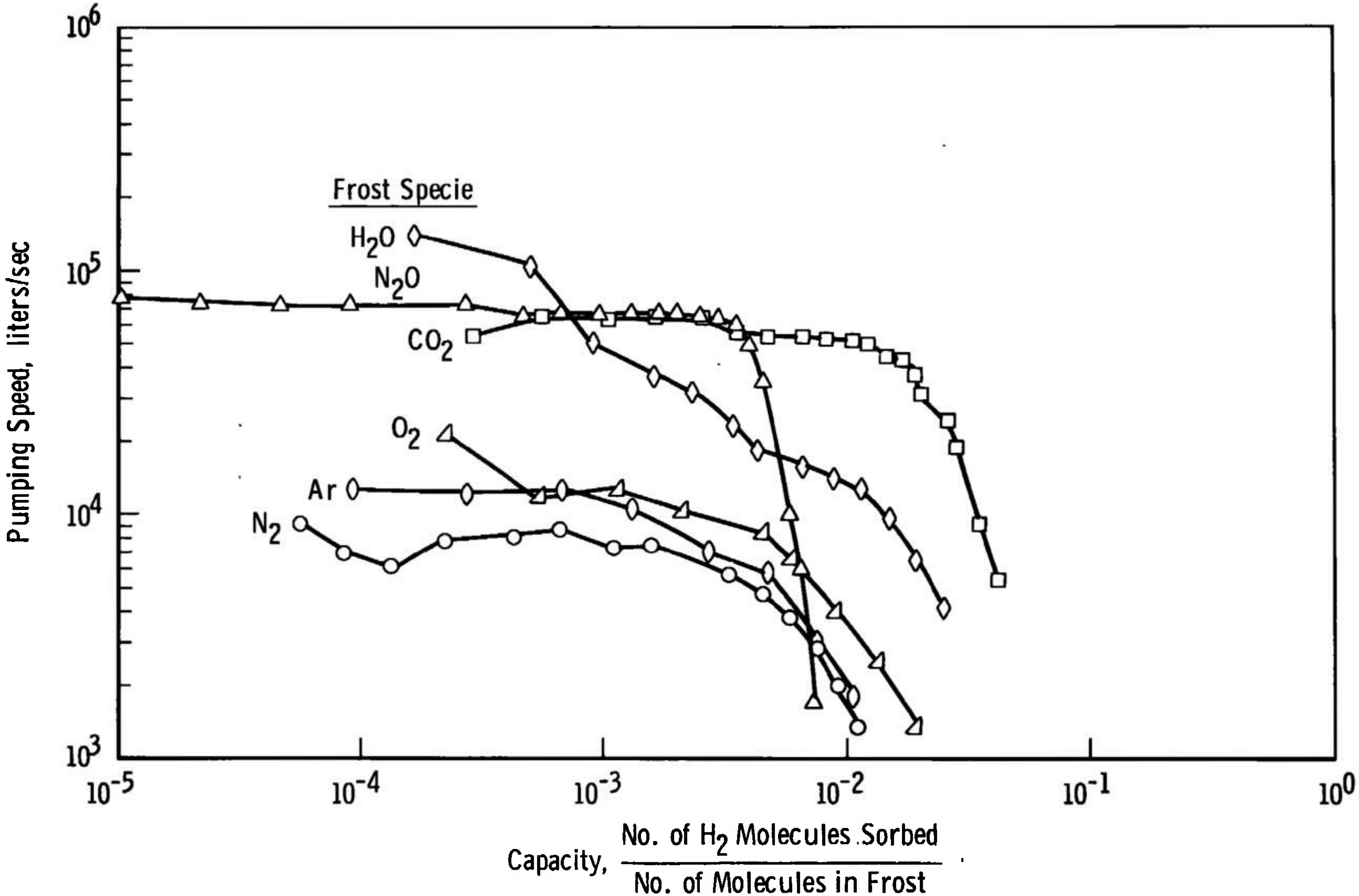


Fig. 1 Frost Cryosorption Measurements of Hunt, Taylor, and Omohundro for 300°K Hydrogen on Various Frosts at 11°K

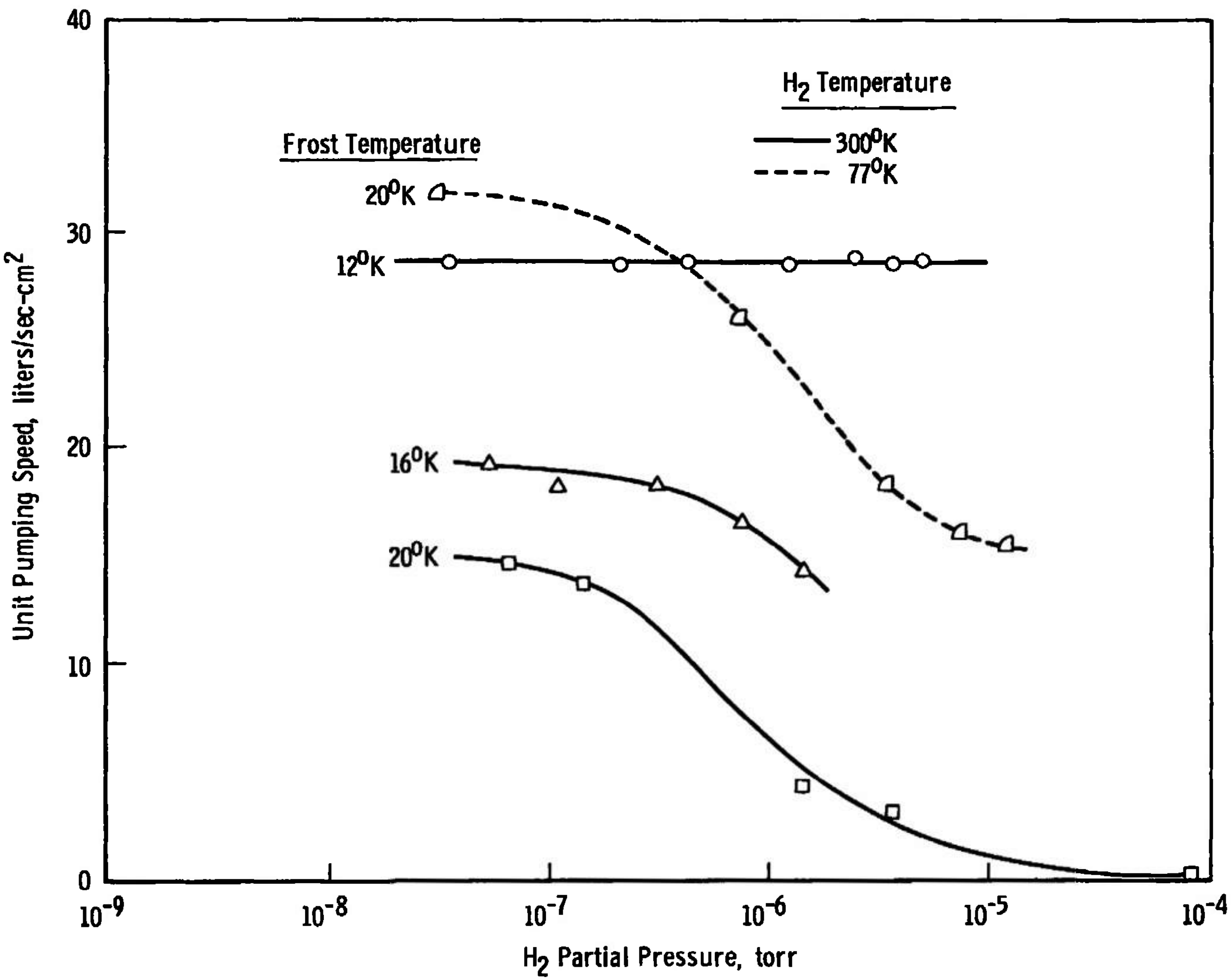
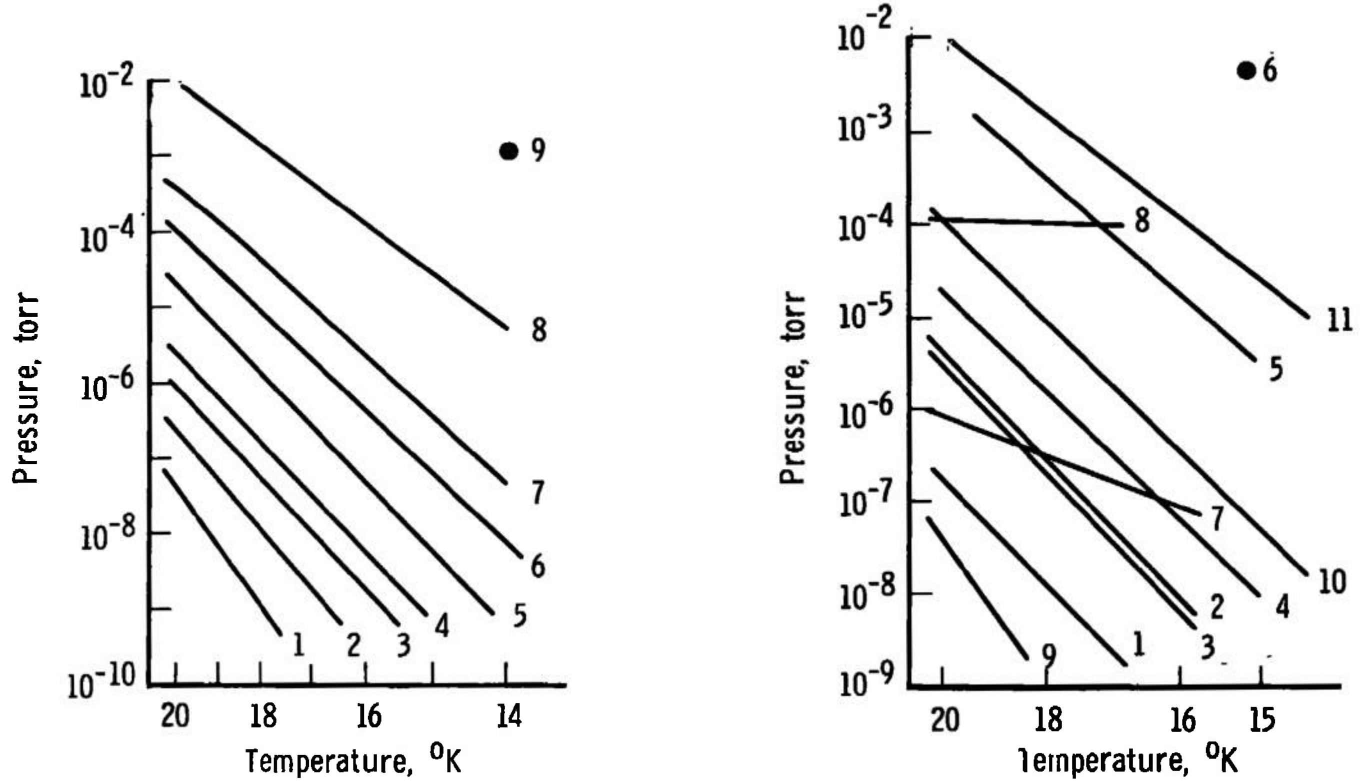


Fig. 2 Hydrogen Pumping Speed Measurements of Dawbarn for Carbon Dioxide Frost at Various Temperatures



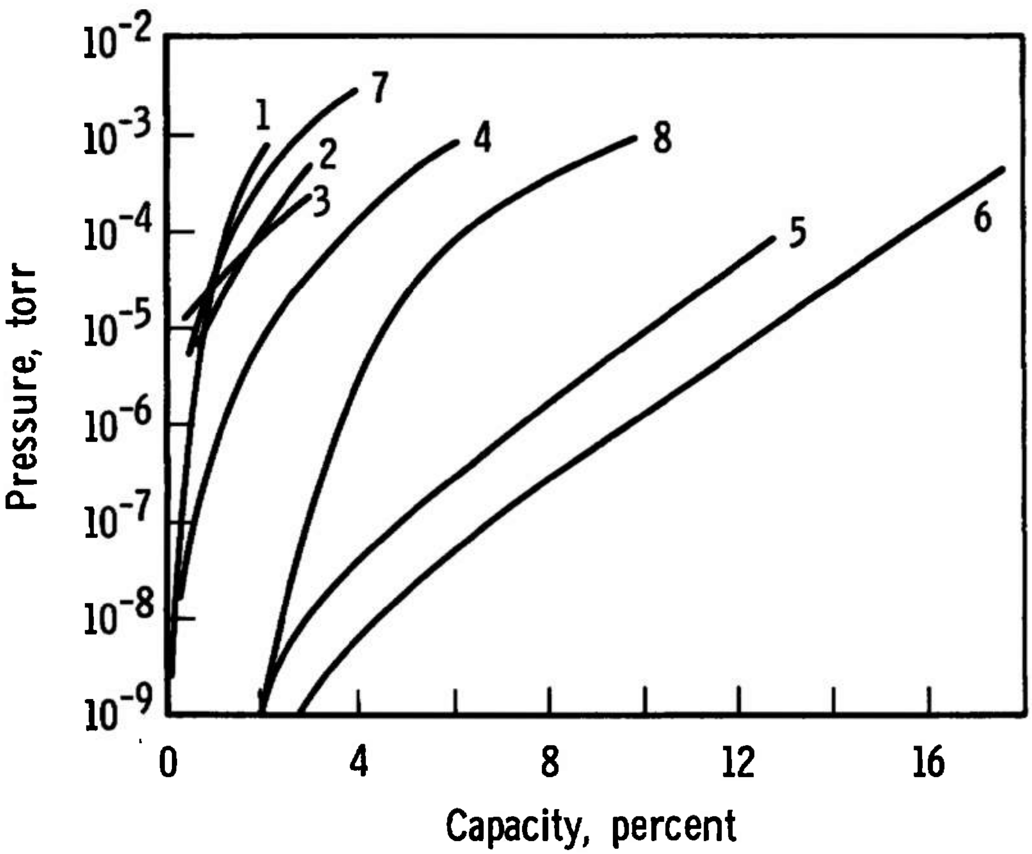
H_2 Capacity in CO_2 Frost, percent

1.	0.4	7.	5.8
2.	0.8	8.	11.3
3.	1.2	9.	18.3
4.	1.6		
5.	2.6		
6.	4.1		

Sorbate-Sorbent Combinations

1. 0.32-percent H_2 in H_2O
2. 0.64-percent H_2 in H_2O
3. 0.5-percent Ne in CO_2
4. 1.0-percent Ne in CO_2
5. 4.1-percent Ne in CO_2
6. 11.8-percent Ne in CO_2
7. 0.4-percent H_2 in N_2
8. 0.4-percent H_2 in Ar
9. 0.4-percent H_2 in CO_2
10. 4.1-percent H_2 in CO_2
11. 11.3-percent H_2 in CO_2

Fig. 3 Isosteres Measured by Yuferov and Busol



Curve	Sorbate	Sorbent	Sorbent Temperature, °K
1	H_2	H_2O	20.4
2	H_2	Alcohol	20.4
3	H_2	Acetone	20.4
4	H_2	CO_2	20.4
5	H_2	CO_2	16
6	H_2	CO_2	14
7	Ne	CO_2	20.4
8	Ne	CO_2	16

Fig. 4 Sorption Isotherms Measured by Yuferov and Busol for 300°K Hydrogen and Neon on Various Frosts

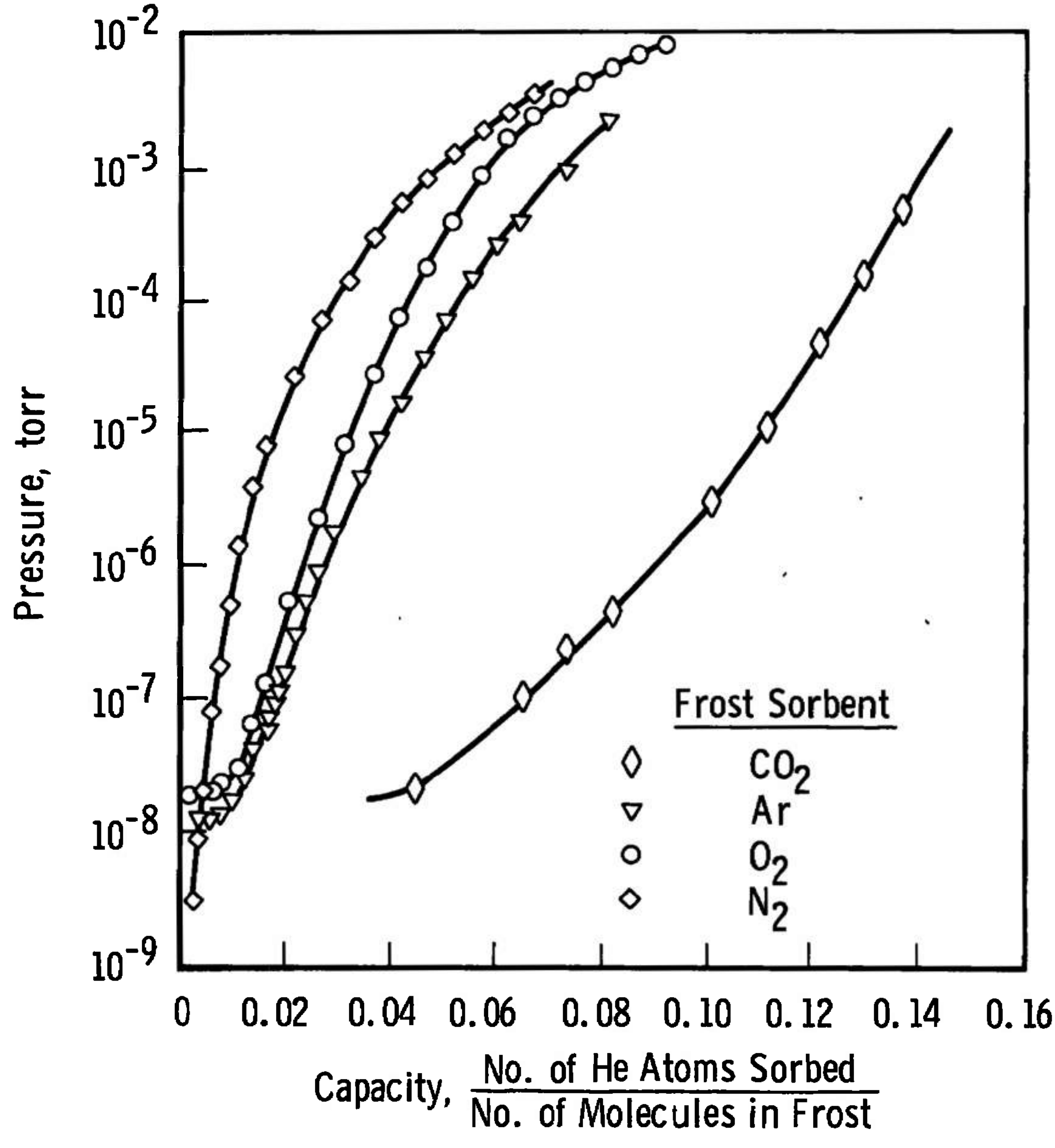


Fig. 5 Sorption Isotherms Measured by Dawbarn and Haygood for 77°K Helium on Various Frosts of 4.2°K (Ref. 8)

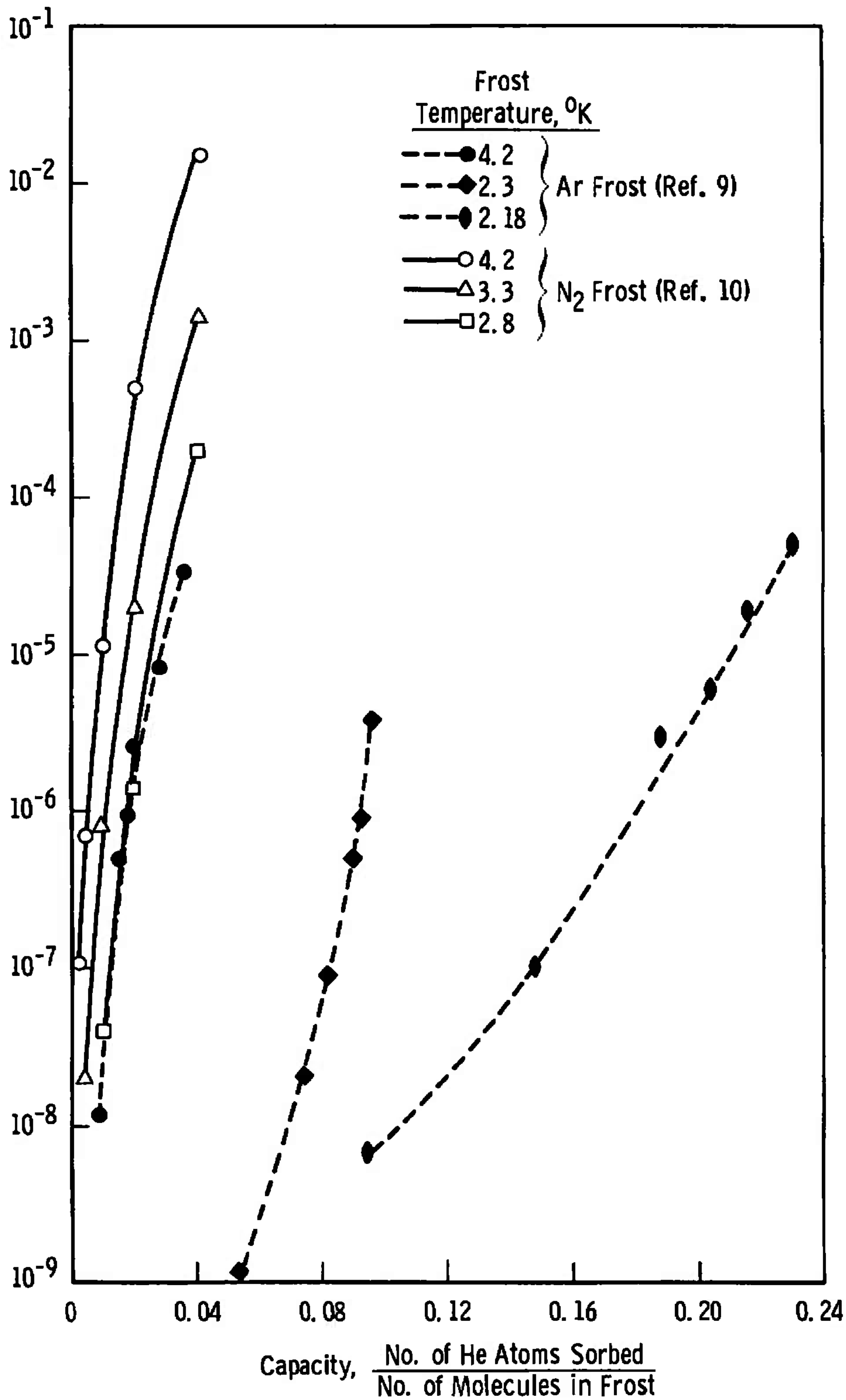


Fig. 6 Comparison of Isotherms for Sorption of Helium on Argon and Nitrogen Frosts at Various Temperatures

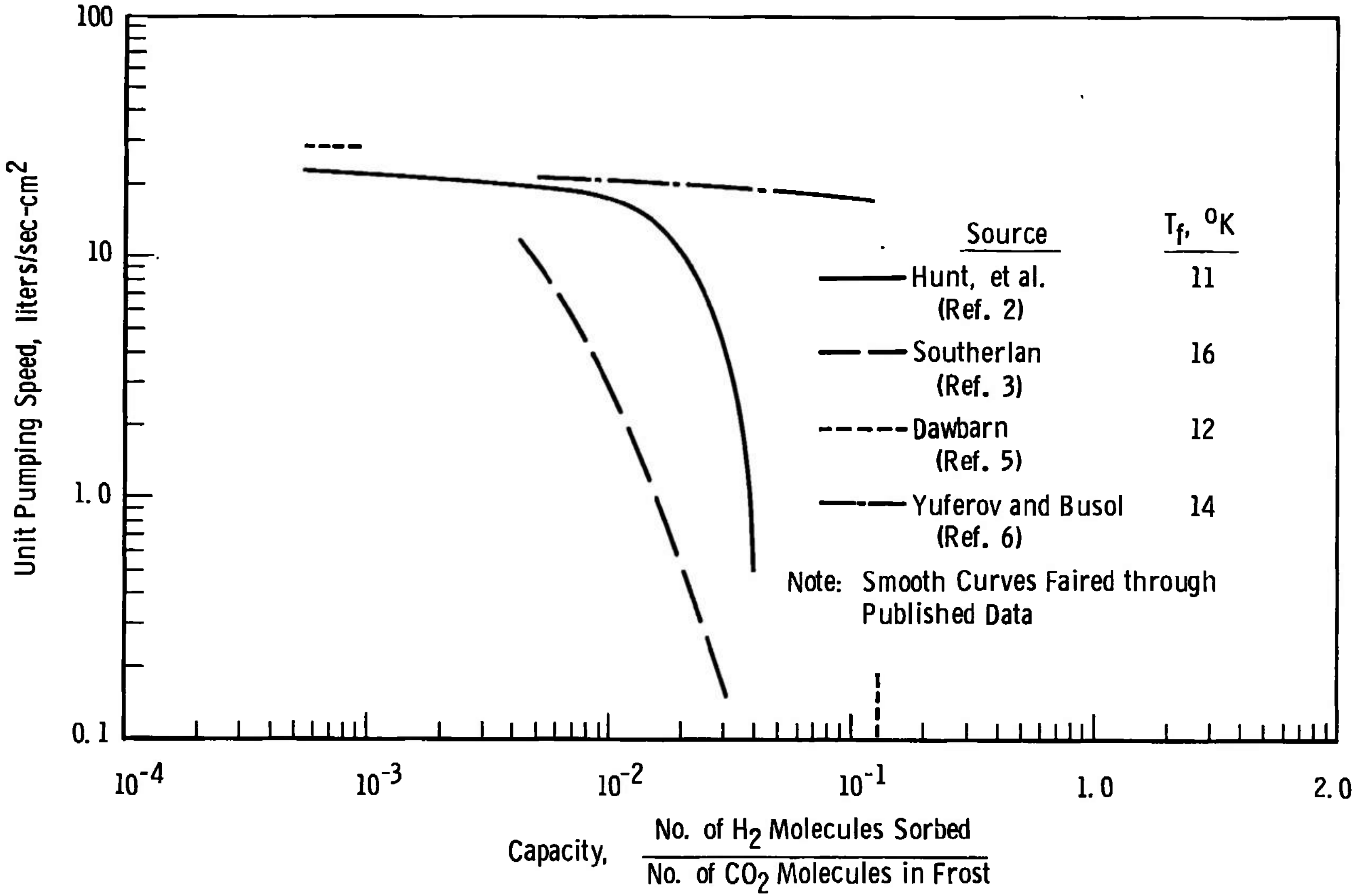


Fig. 7 Comparison of Pumping Effectiveness of Carbon Dioxide Frost for 300°K Hydrogen from Various Investigations

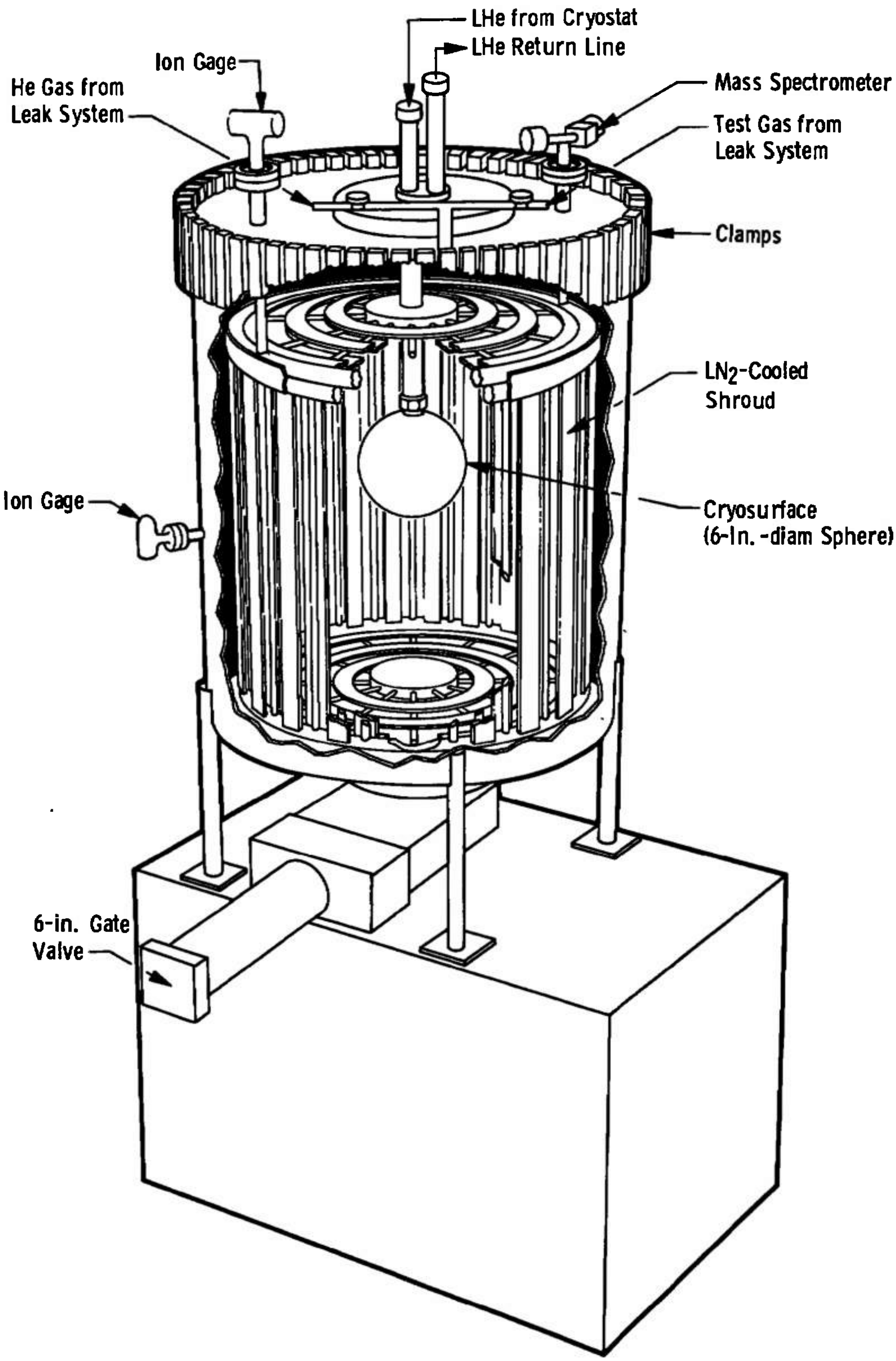


Fig. 8 Schematic of Chamber Used for Hydrogen Cryosorption Tests

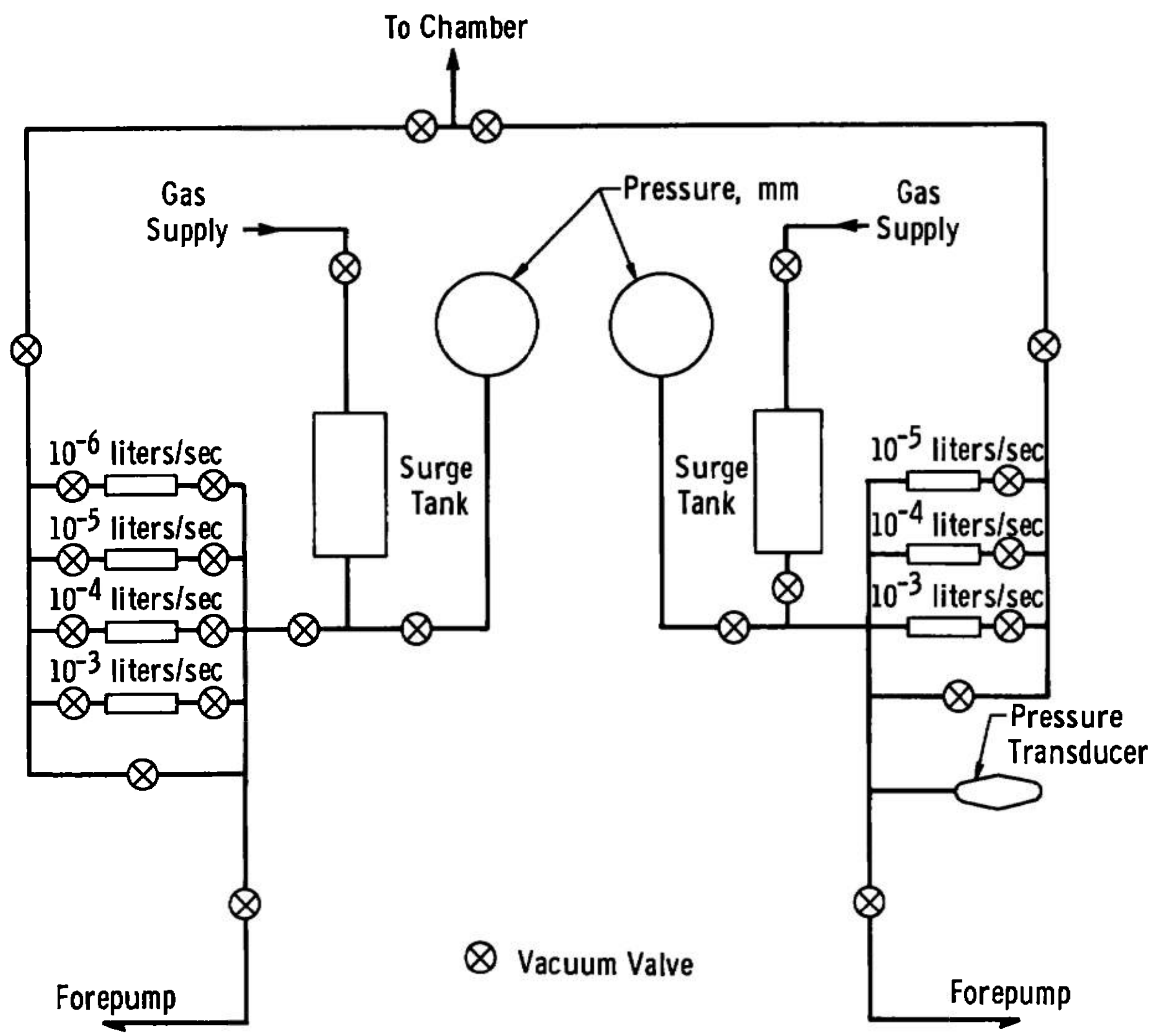
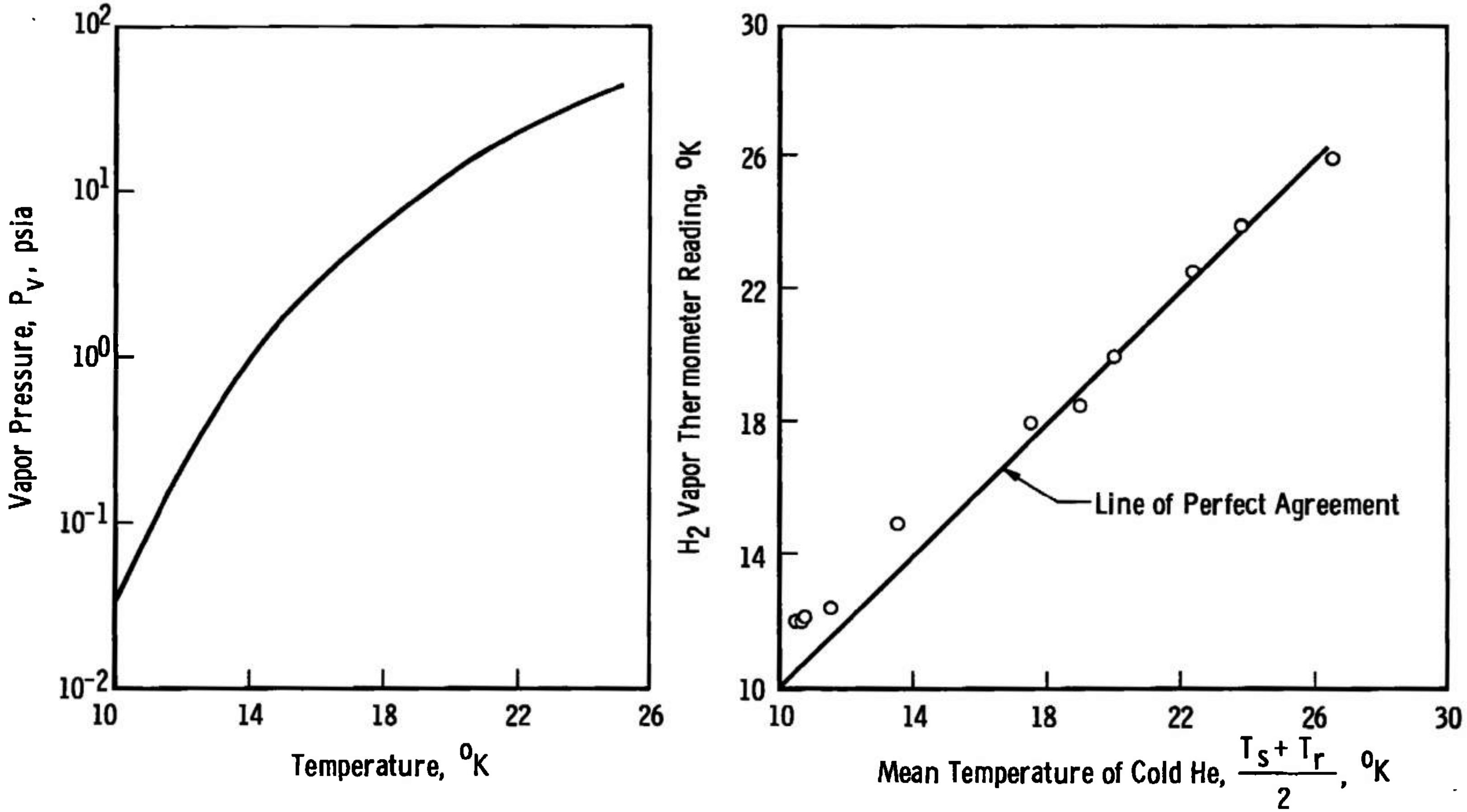


Fig. 9 Gas Addition System



a. H_2 Vapor Pressure Curve

b. Comparison of Measured Temperatures

Fig. 10 Hydrogen Vapor Thermometer Results

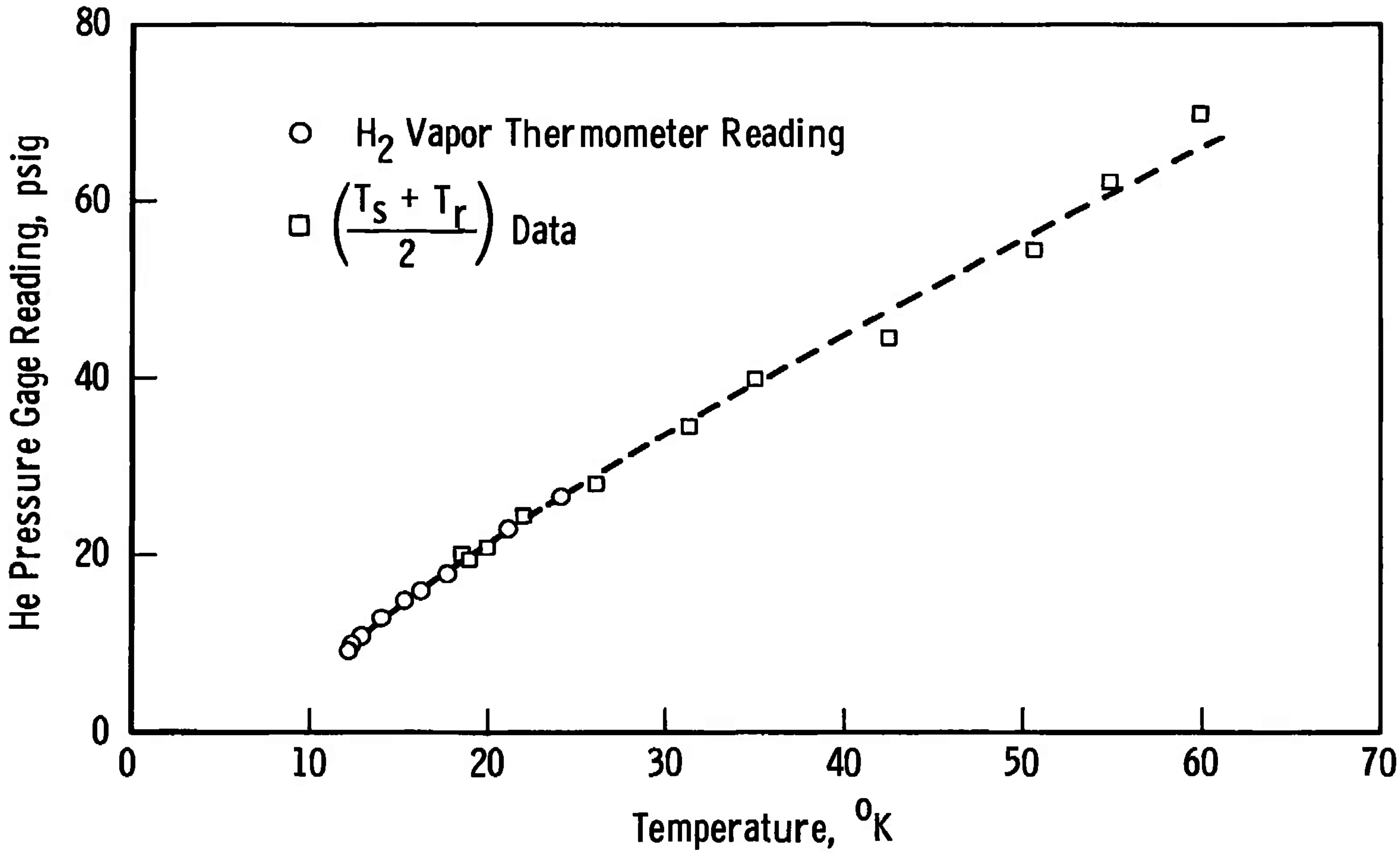
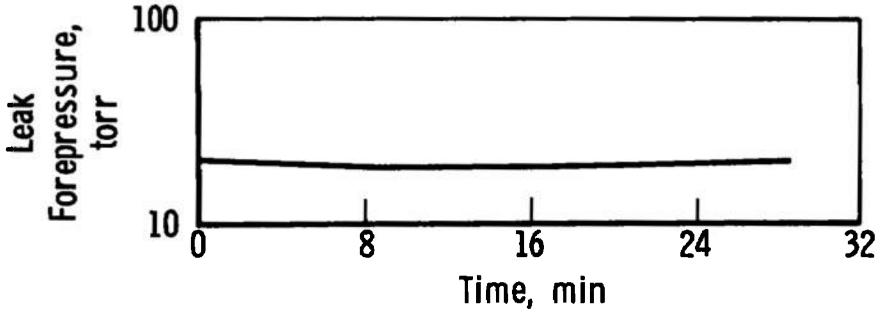
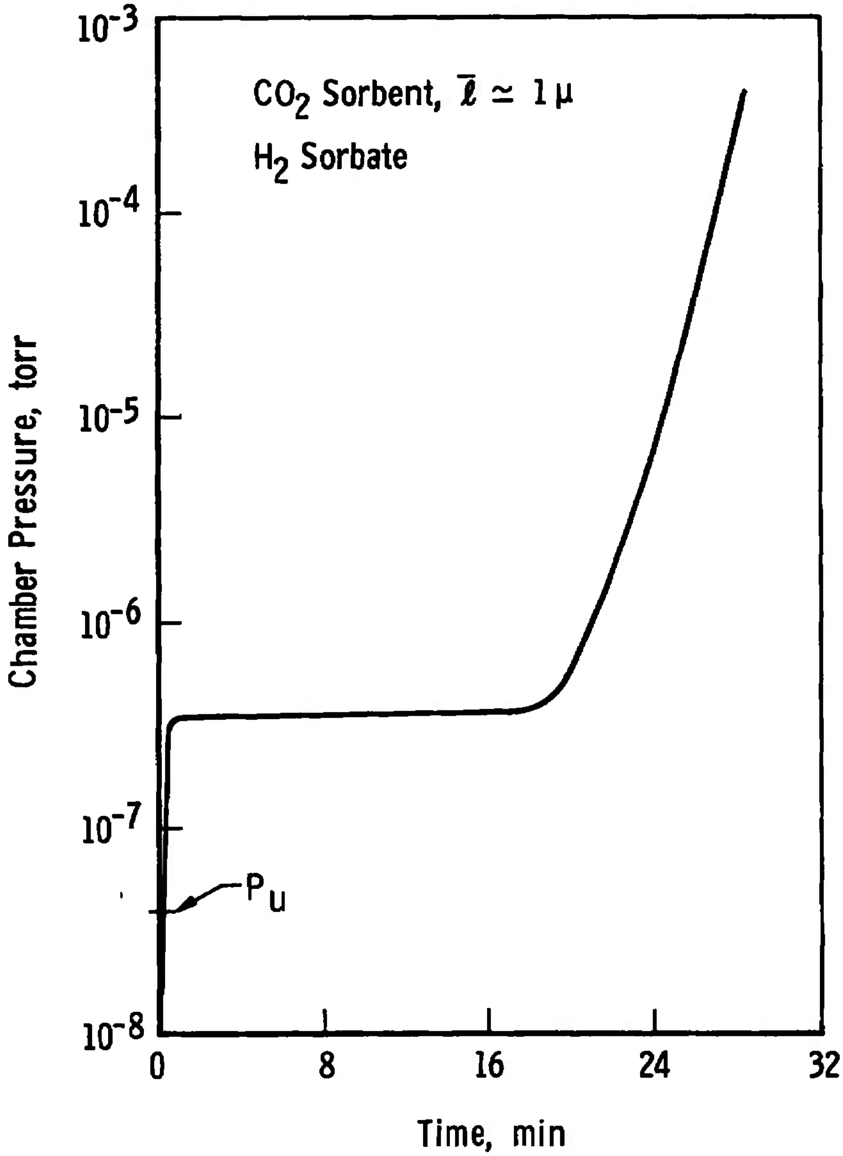


Fig. 11 Calibration Curve for Helium Gas Thermometer



a. Leak Forepressure



b. Chamber Pressure

Fig. 12 Pressure History for a Constant Sorbate Flow Rate Test

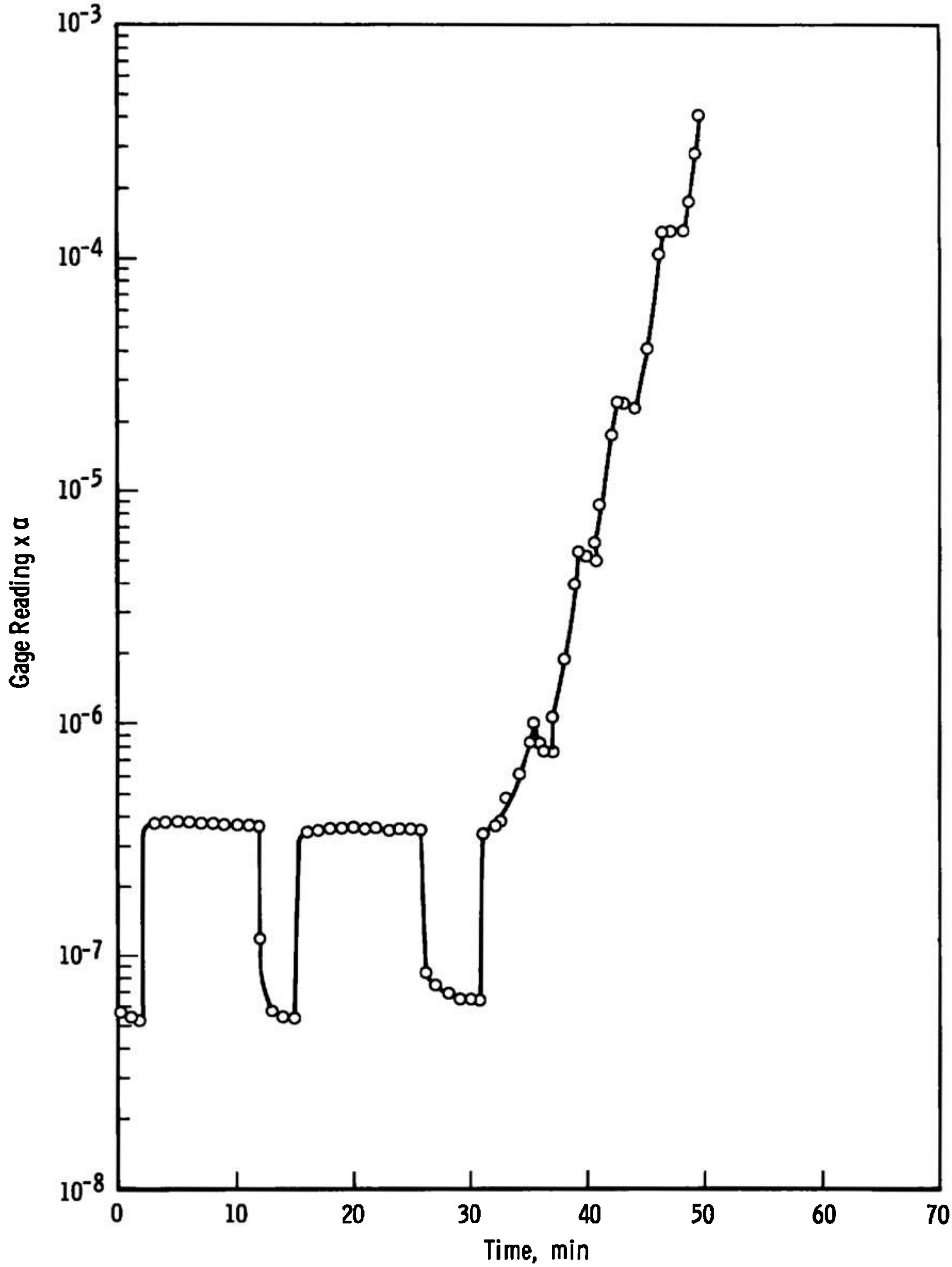


Fig. 13 Hydrogen Pumping by Carbon Dioxide Frost with Interrupted-Inbleed Isotherm Test

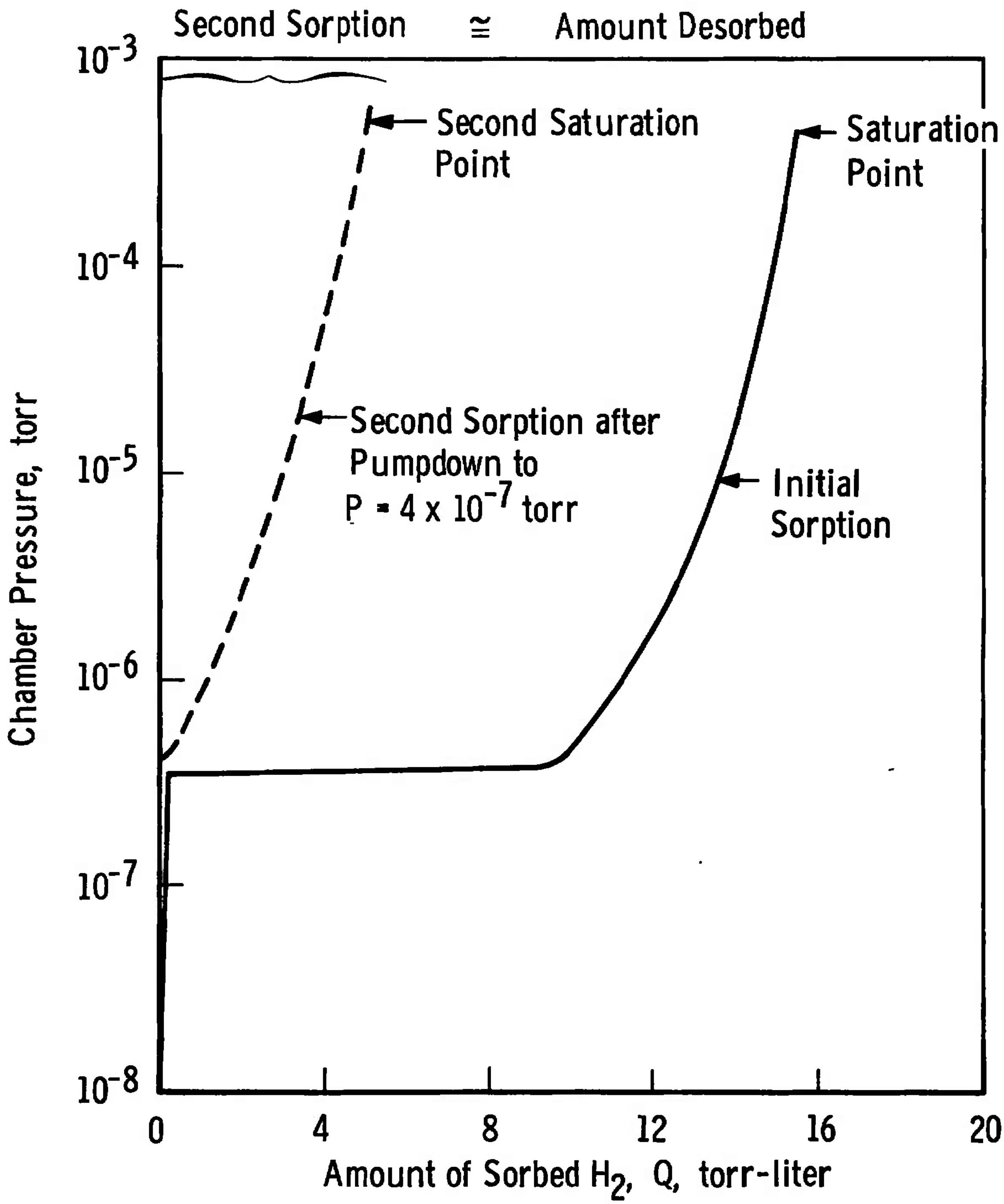
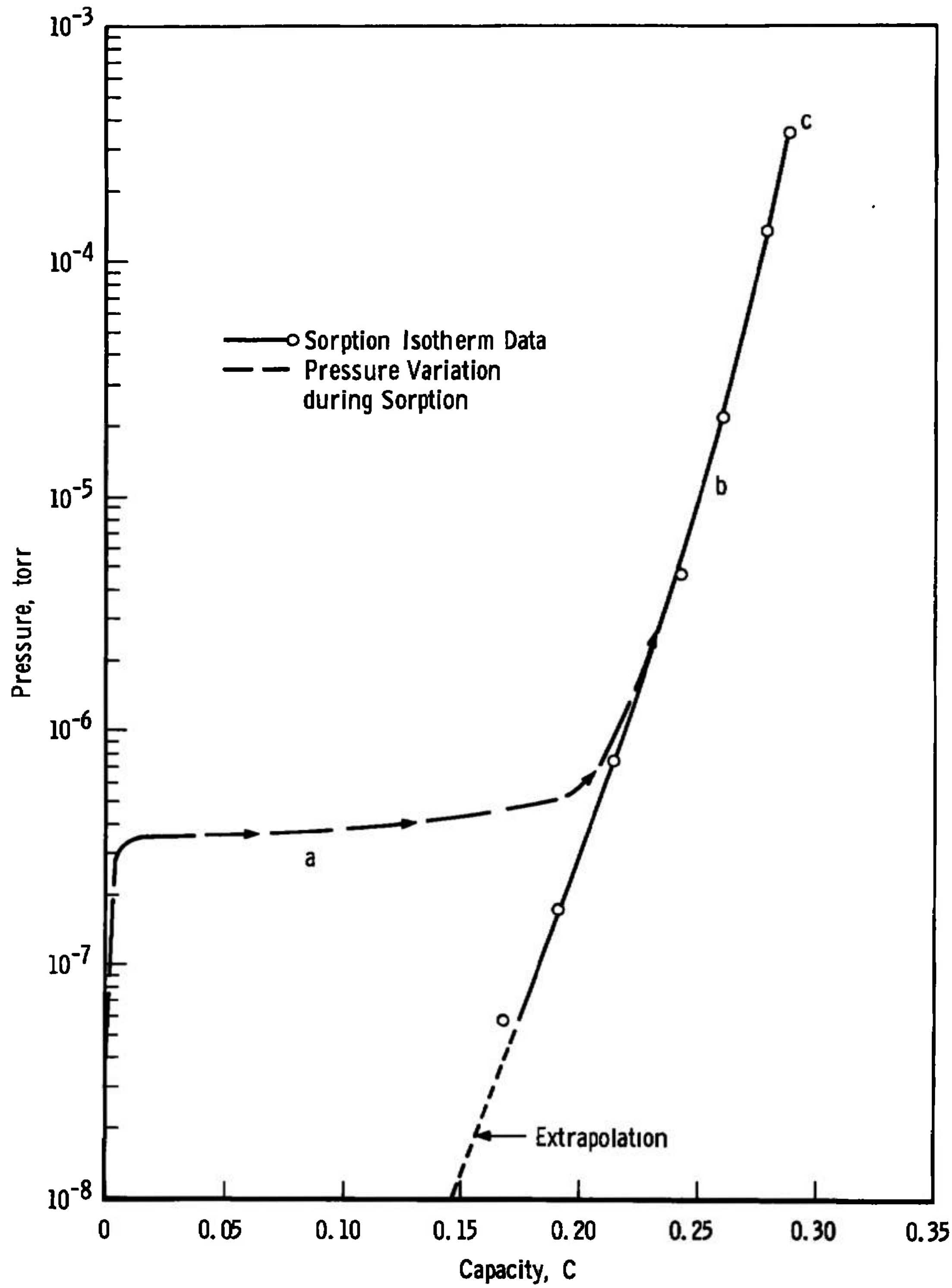
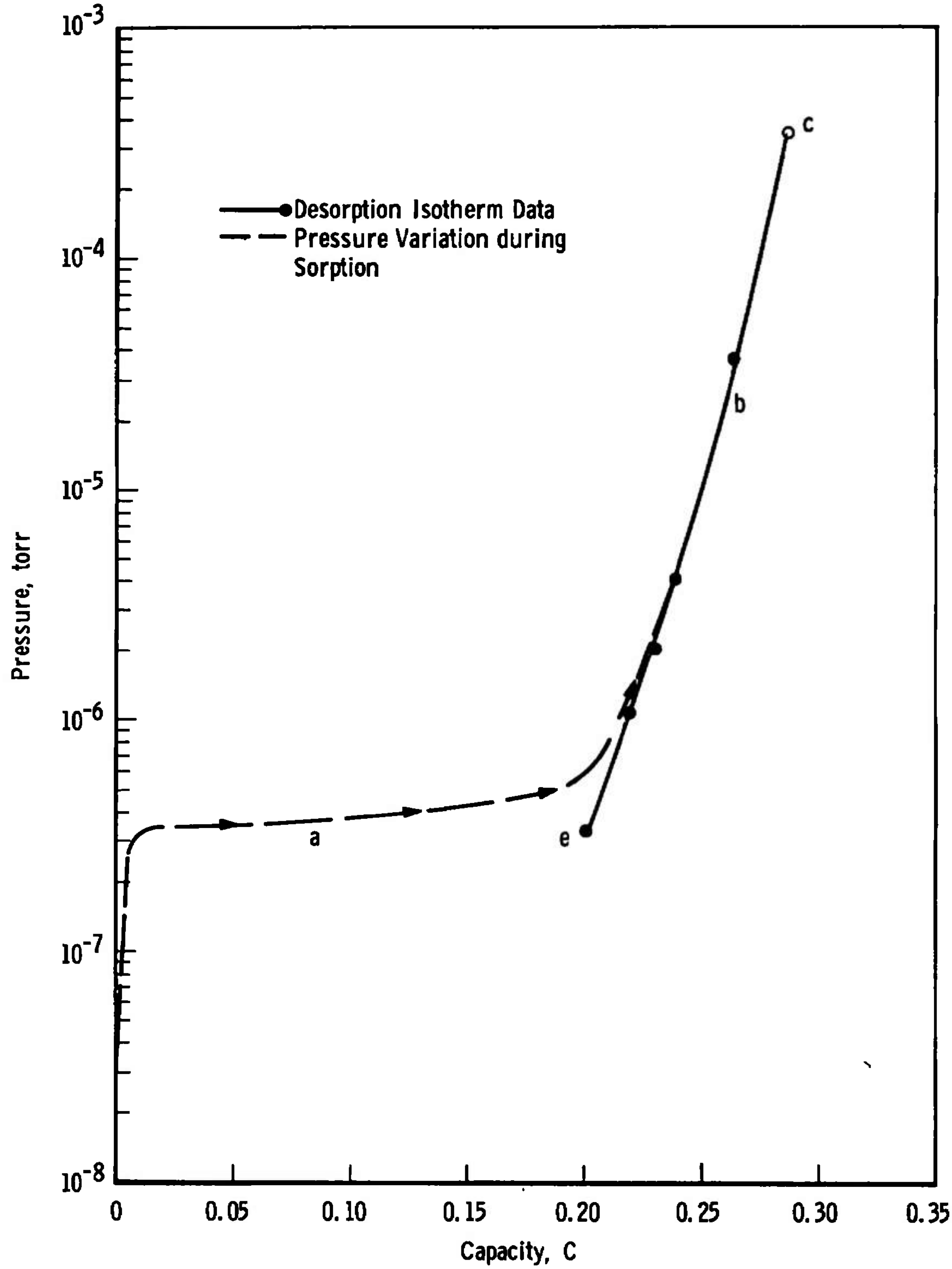


Fig. 14 Typical Desorption Data



a. Sorption Data for Hydrogen on Carbon Dioxide Frost at 12.4°K
Fig. 15 Comparison of Chamber Pressure Variation during Sorption Test with 12.4°K Equilibrium Isotherms



b. Desorption Data for Hydrogen from Carbon Dioxide Frost at 12.4°K
Fig. 15 Concluded

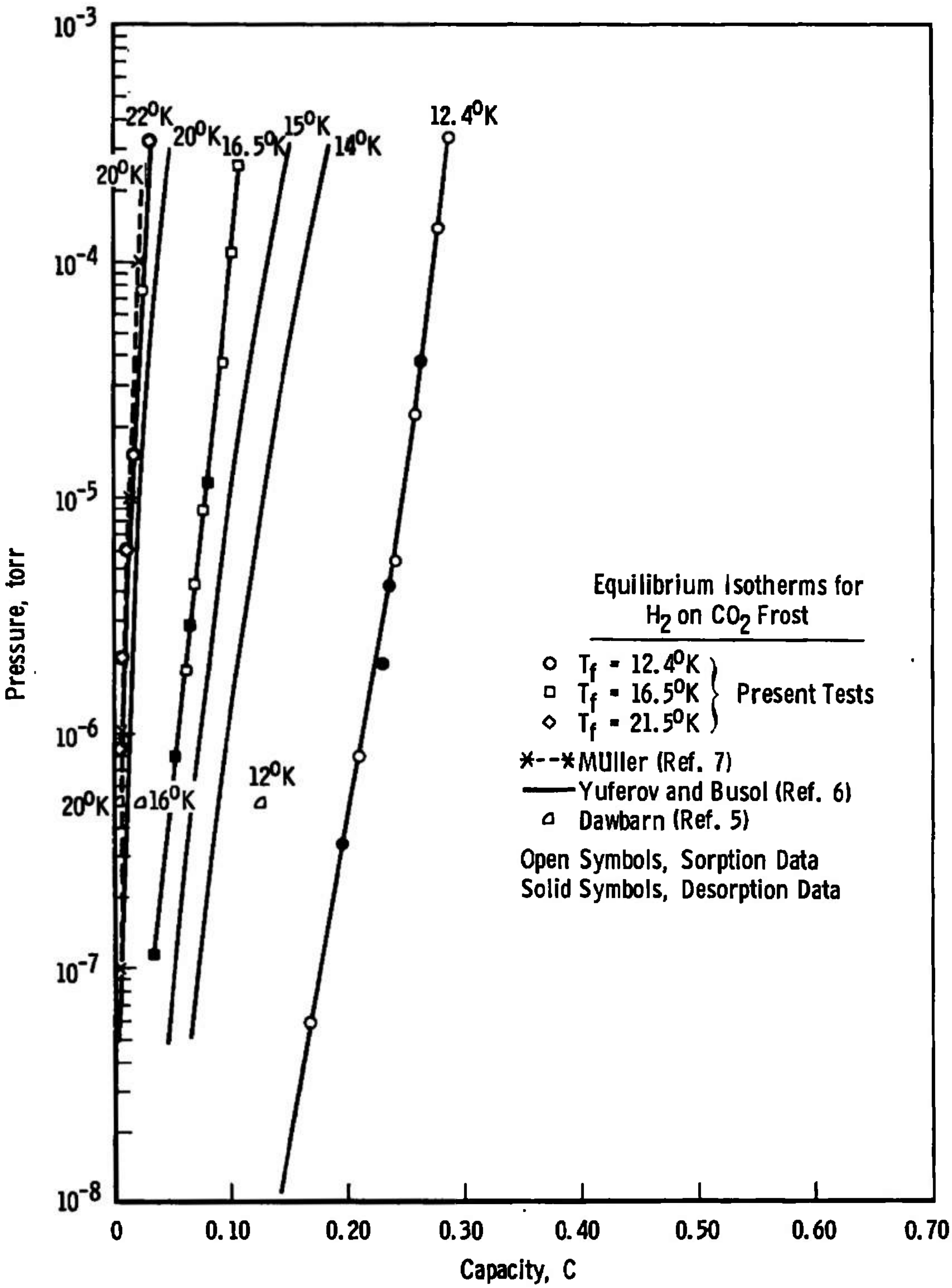
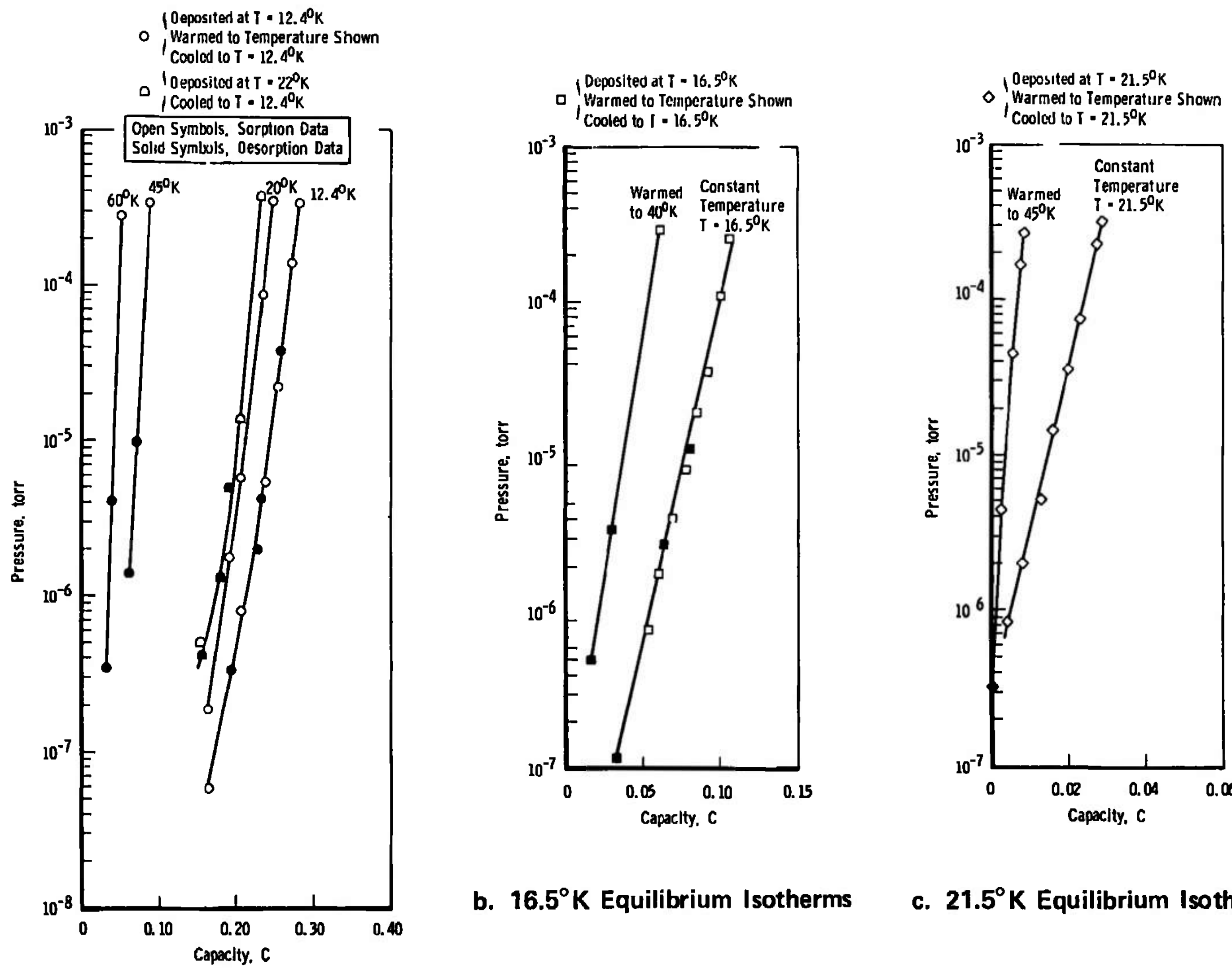


Fig. 16 Comparison of Isotherms for Hydrogen and Carbon Dioxide Frost at Various Temperatures with Those of Other Investigations

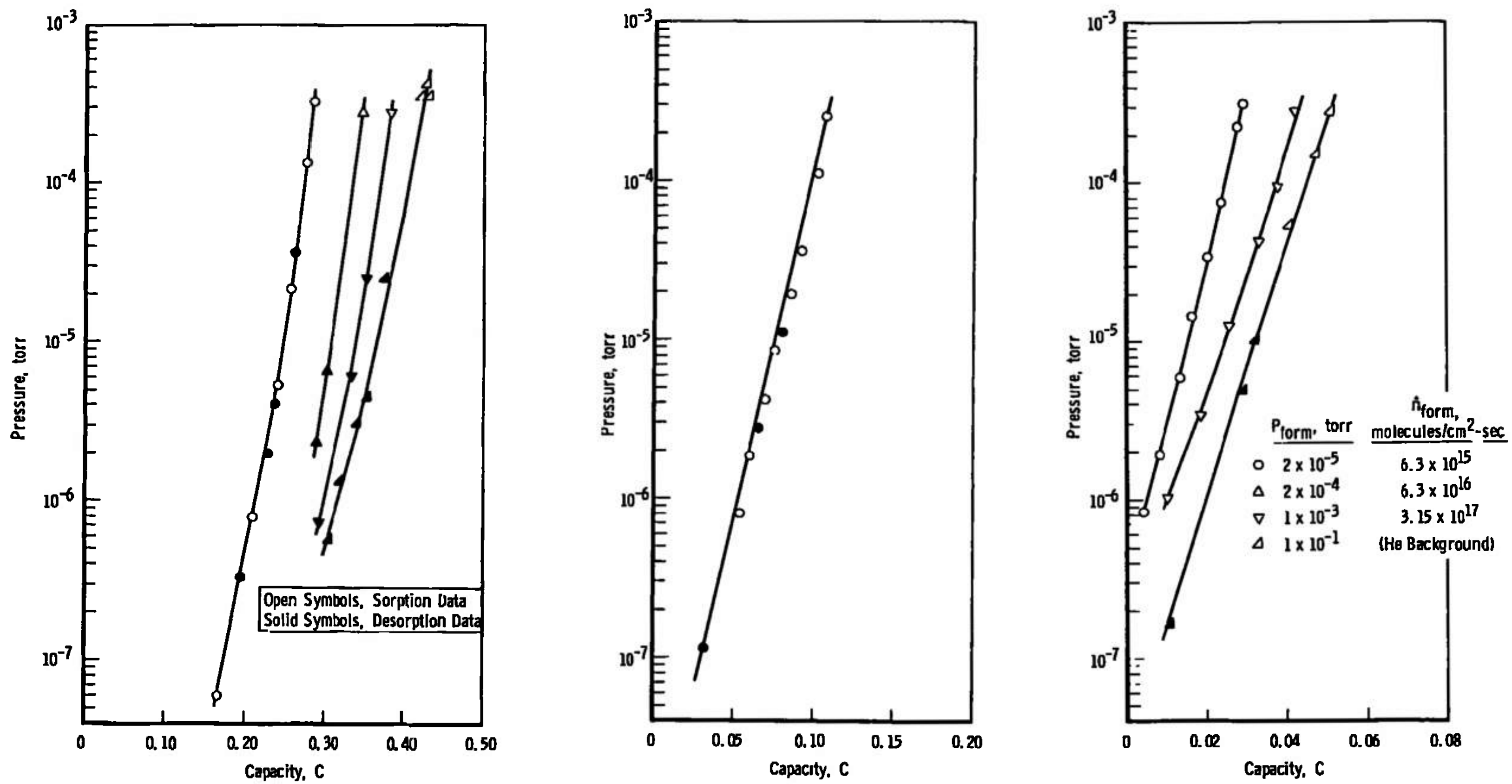


a. 12.4°K Equilibrium Isotherms

b. 16.5°K Equilibrium Isotherms

c. 21.5°K Equilibrium Isotherms

Fig. 17 Effect of a Higher Intervening Temperature on the Hydrogen Sorption Capacity of Carbon Dioxide Frost Deposited at a Strike Rate of 6.15 x 10^{15} molecules/cm^2-sec

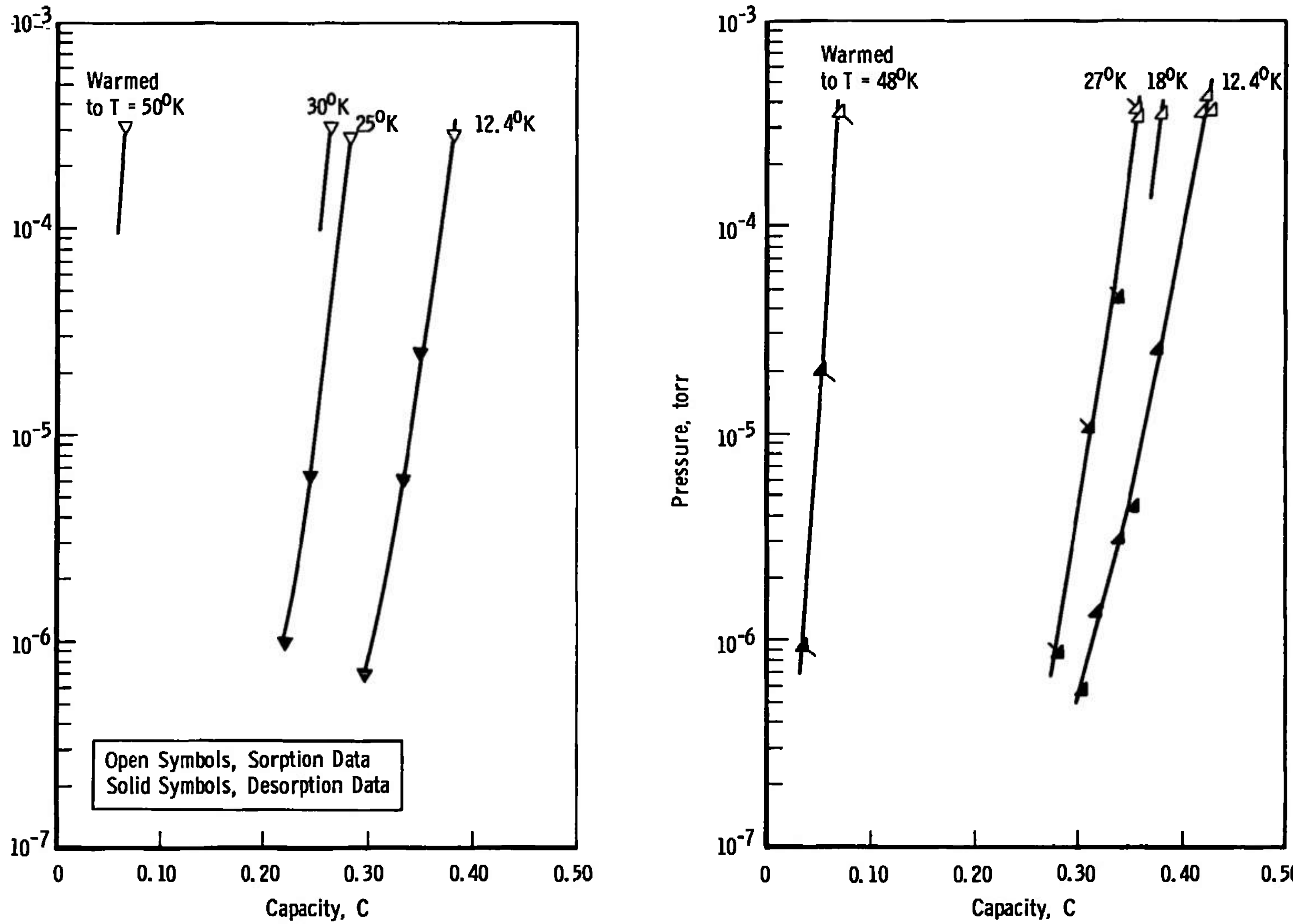


a. 12.4°K Equilibrium Isotherms

b. 16.5°K Equilibrium Isotherms

c. 21.5°K Equilibrium Isotherms

Fig. 18 Effect of Formation Rate on the Hydrogen Sorption Capacity of Carbon Dioxide Frost at Various Temperatures



a. Frost Formed at P = 10^{-3} torr and $\dot{n}$ = 3.15×10^{17} molecules/cm^2-sec

b. Frost Formed in Helium Gas Background of 10^{-1} torr

Fig. 19 Equilibrium Isotherms for Hydrogen on Carbon Dioxide Frost at 12.4°K but Formed at Different Pressure Levels

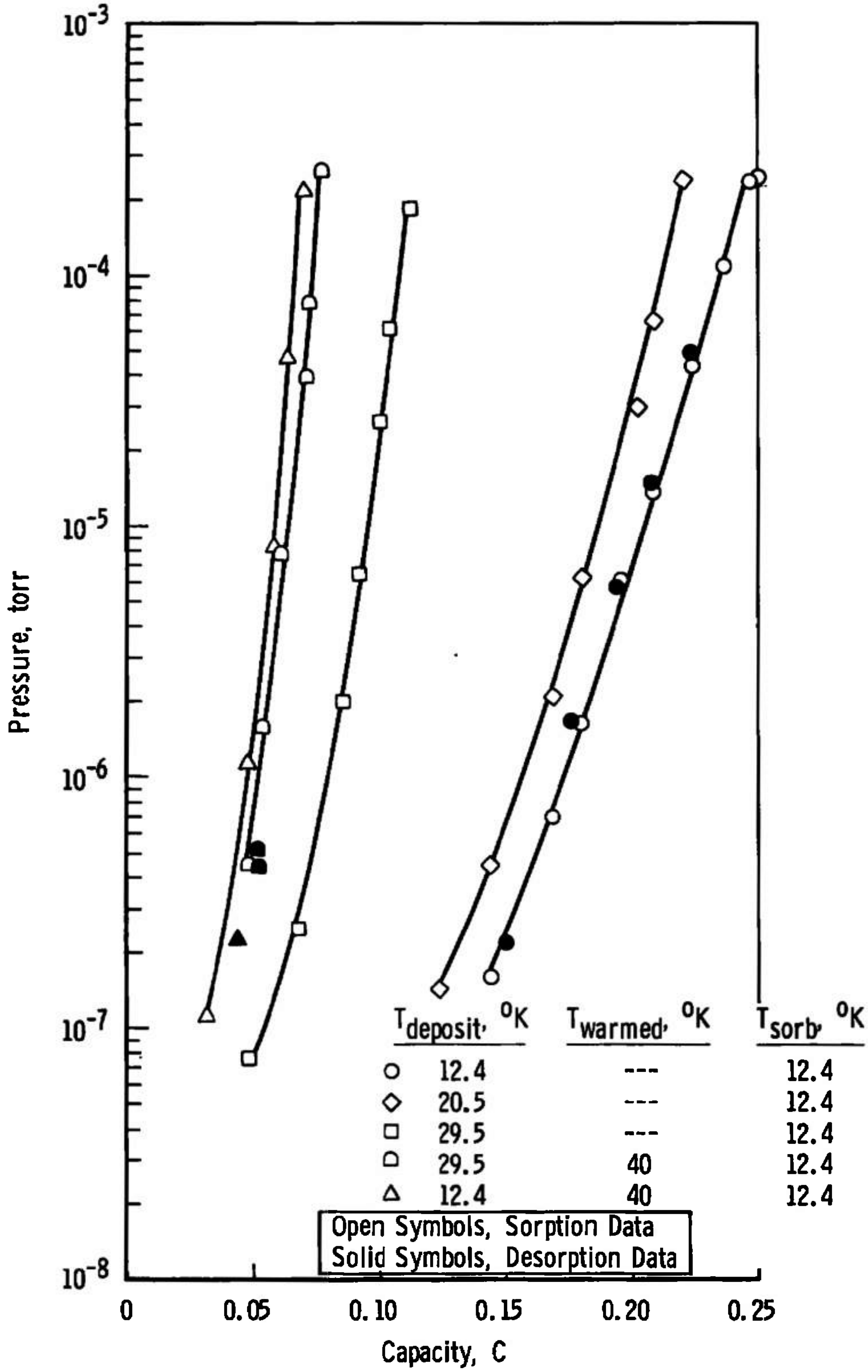
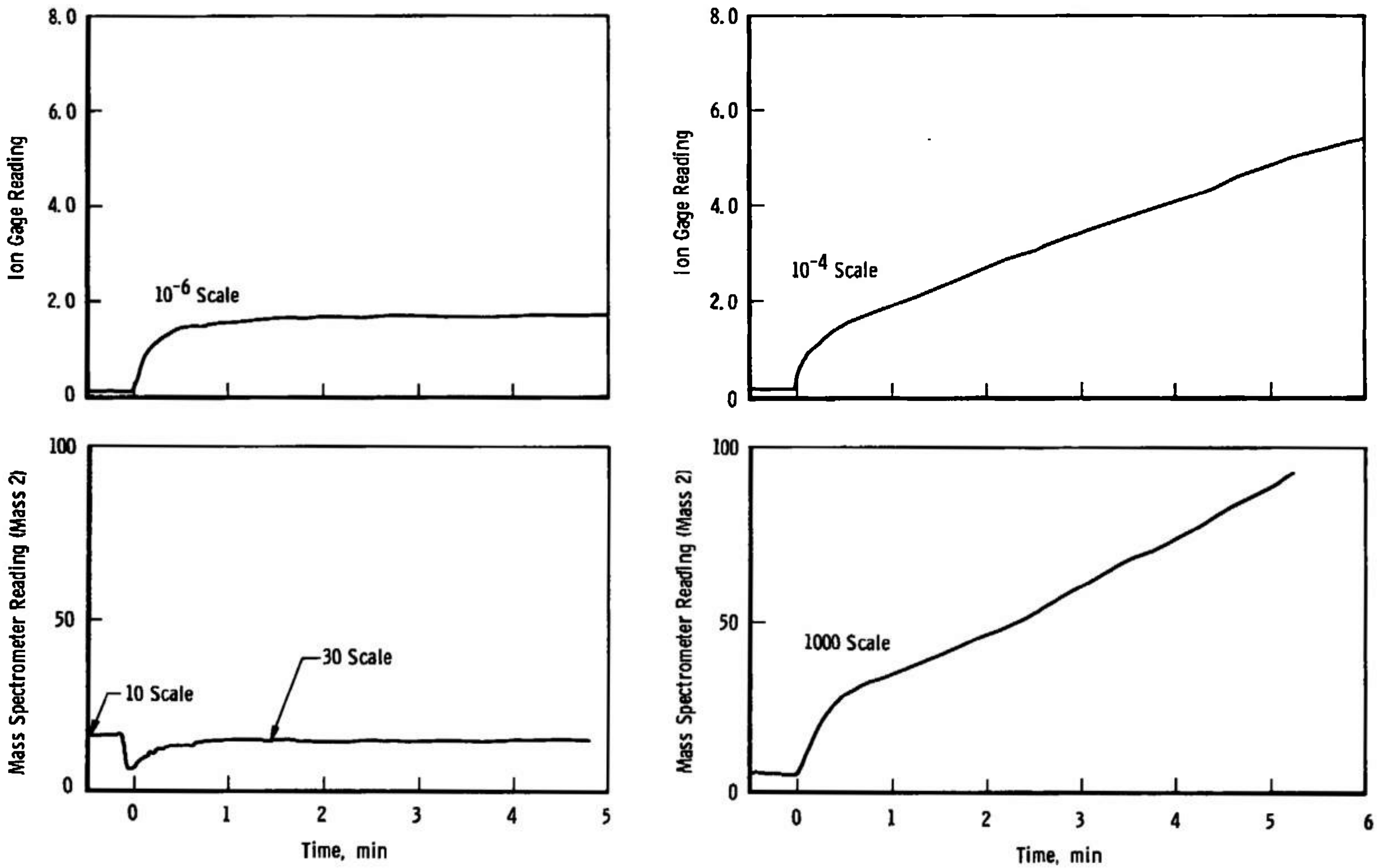


Fig. 20 Equilibrium Isotherms for Hydrogen on Sulphur Dioxide Frost at a Temperature of 12.4°K and Formed at a Strike Rate of 6.3 x 10^{15} molecules/cm^2-sec



a. Chamber Pressure Histories during Carbon Dioxide Sorbent Addition

b. Chamber Pressure Histories during Methyl Chloride Sorbent Addition

Fig. 21 Ion Gage and Mass Spectrometer Readings during Sorbent Gas Additions

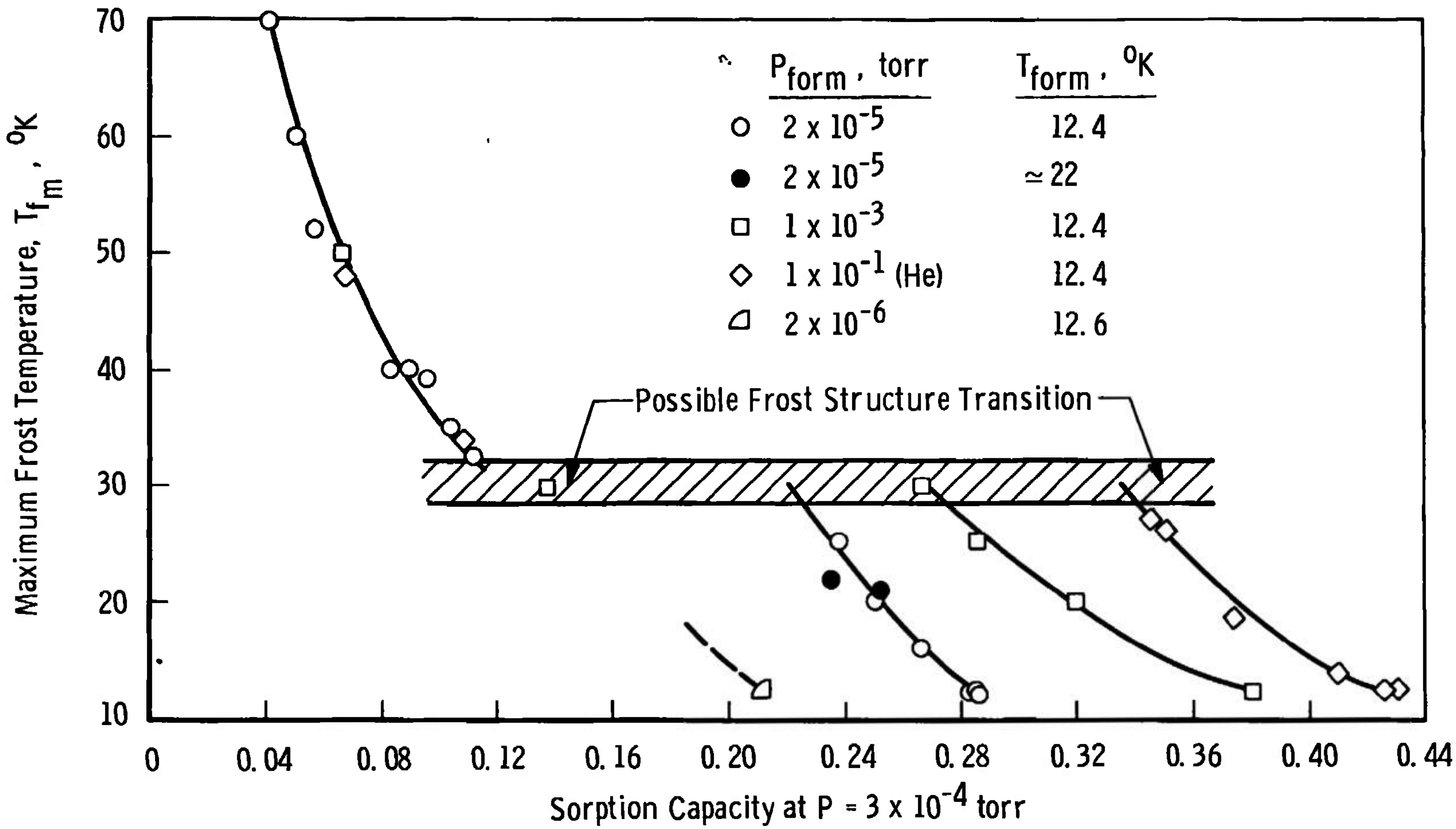


Fig. 22 Near Maximum Sorption Capacity of Carbon Dioxide Frost at a Temperature of 12.4°K as a Function of Intermediate Warming Temperature

APPENDIX II
DEFINITIONS

Inasmuch as the terminology used to describe cryosorption phenomena is not used consistently in the literature and because the similarity of terms can often give rise to confusion, it is appropriate to define a number of processes. These definitions are used consistently in this report.

Adsorption describes a process in which the molecules striking a surface adhere to it and remain for a finite time. Surfaces may be covered with monolayers or multiple layers of molecules because of adsorption.

Absorption will be used to describe the migration of adsorbed molecules away from their adsorption sites and into the interior of the material. Absorption may occur by interstitial diffusion through a crystal structure or by surface diffusion into pores, cracks, and grain boundaries which lead into the interior of the material. Molecules which are adsorbed onto a surface might then be absorbed into the material.

Physical Sorption denotes an adsorption process in which the weak van der Waals attractive forces existing between all substances are responsible for binding the molecule to the surface.

Chemisorption describes an adsorption process in which the forces binding the molecule to the surface are chemical in nature. Chemisorption is believed to occur in two steps. First, molecules are physically adsorbed on the surface, and then they enter into a chemical reaction with the surface and are bound to it chemically as a new compound.

Sorption is often used as a general term to describe adsorption and/or absorption processes where the adsorption may be either physical or chemical. This term is frequently used to represent a combined adsorption-absorption process as well as to describe some sort of adsorption/absorption process which is not well defined.

The **sorbate** is the gas being sorbed by a **sorbent.** For example, in this investigation H_2 is the sorbate while the cryodeposited CO_2 frost is the sorbent.

Cryosorption is used to describe a sorption process in which the sorbent is cooled by a cryogenic fluid.

Cryopumping is the pumping process achieved by condensing a gas onto a cryogenically cooled surface. It is, in effect, a special form of adsorption in which the surface acts as an energy sink, and greatly decreases the probability of desorption.

Cryotrapping is a process in which a noncondensable gas is swept onto a cryosurface by a condensing gas and buried and trapped there by the condensed gas.

The **adsorption energy,** sometimes called the heat of adsorption, is the amount of energy a gas will release to the surface when it is adsorbed. Physical sorption is

characterized by an adsorption energy of a few kcal/mole, while chemisorption involves energies of 10 to 100 kcal/mole.

The **desorption energy** is similarly defined as the amount of energy an adsorbed molecule must acquire before it is energetic enough to leave the surface.

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13. ABSTRACT

The state-of-the-art of cryosorption of hydrogen (H_2) and helium by cold cryodeposited frost is reviewed and summarized in some detail, and the results of additional measurements of the sorption of H_2 by carbon dioxide (CO_2) frosts are reported. It is shown that the sorption capacity of the frost depends upon the conditions at which the frost was formed and upon its temperature history. Frosts formed in a manner to make them porous or disordered are shown to possess greater sorption capacities. It appears that surface diffusion of adsorbed molecules into a disordered frost structure is the basic pumping mechanism. Isotherms for H_2 sorbed by CO_2 frosts formed over a wide range of conditions are presented. Also, the reuse sorption capacity of CO_2 frost is well documented. As a result of the present tests, it is now possible to put the process of frost cryosorption pumping into better perspective and understand the conflicting results of previous experimental investigations.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
sorption						
pumping						
hydrogen						
capacity						
frost						
measurement						

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